THE SODIUM BISULPHITE COMPOUND OF NITROSO β-NAPHTHOL.

by

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THESIS FOR THE DEGREE OF Ph.D.

I N D E X.

INTRODUCTION.

The subject of this research, the sodium bisulphite compound of nitroso β-naphthol, is, surprising as it may seem a bisulphite compound showing little or no relation in its behaviour, to the bisulphite compounds of other organic substances. This will be seen when its properties are dealt with. In spite of the unique position it holds in virtue of its behaviour, which, up till the present has placed it almost in a class by itself, it may be as well to give an outline of the work which has so far been done on the use of bisulphites and sulphites in organic chemistry in general.

The use of the alkali bisulphites, and in particular sodium bisulphite, in organic chemistry, dates from the year 1853 when Bertagnini discovered the reaction of sodium bisulphite with aldehydes (Annalen 1853, 85, 176 and 268.) This work was extended to ketones in the following year, when Limpricht isolated the sodium bisulphite compound of acetone (Annalen 1854, 93, 238.)

From this time onwards, till the year 1891, there is no application of this discovery which is of any importance, and it may be remarked in passing, that even/

even up till the present times all the important applications of the bisulphite reaction have come from aromatic and not aliphatic compounds.

In 1891 Erdmann showed that by using neutral sodium sulphite, it was possible to replace a chlorine atom in a benzene ring which contained other substituents (D.R.P. 65,240). In addition to the replacement of the chlorine atom by a sulphonic group, the reduction of a nitro group, if it is present, may take place. Thus a convenient method for the preparation of amino sulphonic acids is available. Nietzki and Helbach (Ber. 1896, 29, 2448 and D.R.P. 86,097) showed that the presence of an easily replaceable chlorine atom is not necessary for the introduction of the sulphonic group. While this is true, nevertheless, the yield is poor, so that the direct introduction of a sulphonic group into a benzene ring by means of sodium sulphite is not a practical proposition.

It was in 1904 that the use of bisulphites in preparative organic chemistry received its greatest impetus. In that year Bucherer published two papers (J. pr. Ch. 1904, 69, 49 and 1904, 70, 345.). In these two papers he showed that it was easy to convert naphthols into naphthylamines and the reverse, naphthylamines into naphthols, by means of ammonium bisulphite and ammonia, and sodium bisulphite and water respectively. Bucherer also indicated the formation/

formation of a sulphite ester as an intermediate product in each case. If we represent a naphthalene molecule by R these reactions may be represented as follows

(a) $R \cdot OH \xrightarrow{(NH_4)_2SO_3} R \cdot O \cdot SO_2 \cdot NH_4 \xrightarrow{NH_3} R \cdot NH_2$

(b) $R \cdot NH_2 \xrightarrow{NaHSO_3} R \cdot O \cdot SO_2Na \xrightarrow{H_2O} R \cdot OH$

It should be noted that there appeared to be some difference of opinion about the constitution of the ammonium sulphite ester which is the intermediate compound between the naphthol and the naphthylamine. This might be expected in the light of later research which has shown that it does not exist in any of the forms favoured by Bucherer and his collaborators.

The great importance of these reactions lies of course in the importance of the end products, naphthylamines and naphthols. Previous to the use of ammonium sulphite, the reaction had to be carried out under a pressure of 60-70 atmospheres, and even then the yield was not good. Bucherer then extended the reaction, using amino compounds instead of ammonia. For instance, phenyl β-naphthylamine 6-sulphonic acid can be produced by heating together, sodium β-naphthol 6-sulphonate, aniline and sodium bisulphite. (D.R.P. 122,570). Mono and dialkylated amines were found to/

to react in the same way, giving in the presence of sulphite, naphthol sulphites, and eventually naphthols, when further treated with water or alkalies. The reverse reaction, the formation of secondary or tertiary amines by the action of the primary or secondary amine and its sulphite, does not take place nearly so readily as the corresponding ammonia reaction (Bucherer loc. cit.). Bucherer also found that benzenoid amines and phenols with the exception of m-diamino and m-dihydroxy compounds, do not give these reactions, and in the case of the two latter types of compounds, the reaction is complicated.

Bucherer's view of the course of the reaction to which he gives his name remained unchallenged until 1915 when Woroshtzow examined the reaction between bisulphites and derivatives of naphthols (J. Russ. Chem. Soc. 1915, 47 1669, and Annales de Chemie 1916, 6, 386). In particular, he examined 1:5 and 1:8 naphthols and 1:5 and 1:8 amino naphthols. In both these cases he came to a different conclusion as to the formula, from that put forward by Bucherer. He found in each case a molecule more of water. There was some doubt, however, in the case of the naphthol sulphonates which form bisulphite compounds, whether or not some of them, did not give a bisulphite compound of the ester or Bucherer type. Thus, 1:4 naphthol sulphonic acid appeared to confirm Woroshtzow's view/

view about the reaction being an additive one, while the 1:5 and 1:8 naphthol sulphonic acids apparently agreed with the ester structure. In those cases, however, in which the ester formula seemed the correct one, the bisulphite compound had been formed by boiling the acid with the bisulphite solution. To settle this matter Woroshtzow (Ber. 1929, 62, 57) prepared the bisulphite compounds of those acids which would give them in the cold, (the 1:4 and the 2:1 acids for instance) and in no case did he find any indication of the ester type of formula. In addition to this, the sodium bisulphite compounds of the benzene azo β-naphthol compounds, which are known to be formed by simple addition, Woroshtzow:(J. Russ. Phys. Chem. Soc. 1911, 43, 771, and 1915, 47, 1669) show a remarkable resemblance in properties to the bisulphite compounds of the naphthol sulphonic acids. To clinch the matter, however, the same idea of addition without elimination of water has been arrived at by the following workers, quite independently, (P. Friedlander Ber. 1921, 54 620; König and Haller. J. pr. Ch. 1920, 101, 43; Fuchs. Ber. 1922, 55 662.)
The theory of course applies equally to the action of bisulphite on naphthylamines. We therefore have the following reactions, instead of the Bucherer reactions, which have already been given, but which are again included here, for comparison.

$R \cdot OH \longrightarrow R \cdot O \cdot SO_2 \cdot NH_4 \longrightarrow R \cdot NH_2$ (Bucherer)

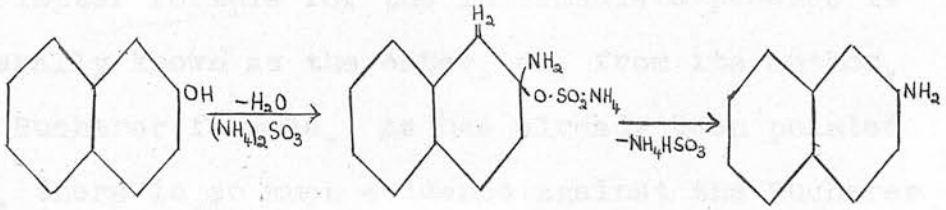
$R \cdot OH \longrightarrow RH \cdot NH_2 \cdot O \cdot SO_2 \cdot NH_4 \longrightarrow R \cdot NH_2$ (Woroshtzow)

$R \cdot NH_2 \longrightarrow R \cdot O \cdot SO_2 \cdot NH_4 \longrightarrow R \cdot OH$ (Bucherer)

$R \cdot NH_2 \longrightarrow RH \cdot (OH) \cdot O \cdot SO_2 \cdot NH_4 \longrightarrow R \cdot OH$ (Woroshtzow)

To take a specific case we will examine the reactions of β-naphthol with ammonium sulphite, and β-naphthylamine with sulphurous acid respectively. According to Woroshtzow the reactions are as follows.

(a)



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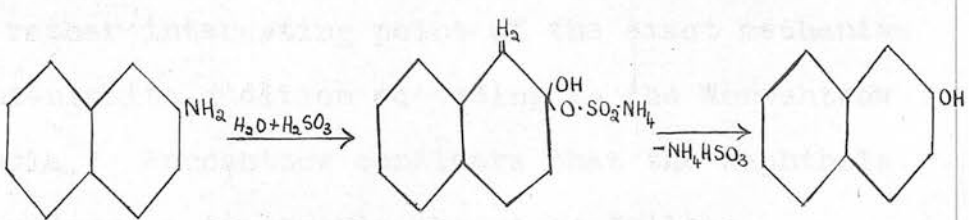
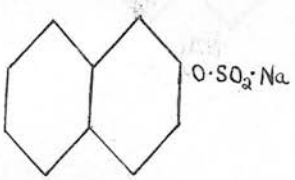
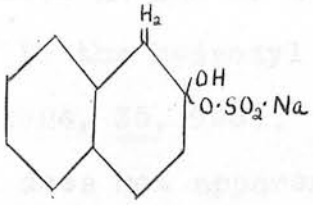


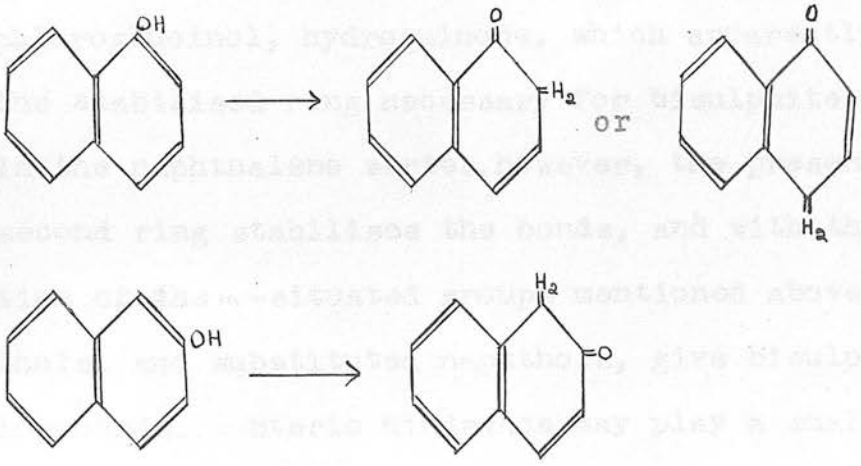
The essential point is the structure of the intermediate compound which is quite different from that put forward by Bucherer. Considering again β-naphthol, Bucherer stated that the first action of sodium bisulphite was to form a compound



While Woroshtzow, and the others mentioned on p. 5 say that the intermediate compound has the constitution



one of course, is an addition product, and the other is formed by the elimination of a molecule of water. The latter formula for the intermediate product is generally known as the ester, or, from its author, the Bucherer formula. As has already been pointed out, there is so much evidence against the Bucherer formula that it must be abandoned, and this leads to the rather interesting point of the exact mechanism of bisulphite addition according to the Woroshtzow formula. Woroshtzow considers that the naphthols can undergo a tautomeric change as follows.



These tautomeric changes shown above are supposed to occur with all derivatives of the naphthols, except those in which an azo or sulphonic group occupies a m-position to the hydroxyl group. Woroshtzow (Bull.Chem. Soc. 1924, 35, 996). In this case bisulphite addition does not apparently take place. The theory underlying this is, that for the tautomeric change to take place, the system of double bonds must be stablished. When this is achieved the stabilised ring becomes enolic in character, and of the nature of a cycloolefine, in which state addition can take place. In other words, a hydroxyl group is supposed to be enolic when it is situated beside a stable double bond. Those compounds therefore, which fall into this class, can give bisulphite compounds and the others cannot. In general, Woroshtzow finds that phenols, with the exception of resorcinol, do not fulfil the necessary conditions, but it will be shown later that there are certain phenols, e.g. resorcinol, phloroglucinol, hydroquinone, which apparently have the stabilised ring necessary for bisulphite addition. In the naphthalene series, however, the presence of a second ring stabilises the bonds, and with the exception of the m-situated groups mentioned above, naphthols, and substituted naphthols, give bisulphite compounds. Steric hindrance may play a small part in/

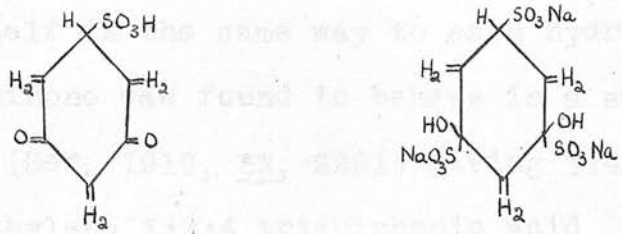
in some cases, but this will be dealt with in the discussion of results. A complete account of the theory is given in the Bulletin de la Société Chimique à Paris 1924, 35, 1004.

This theory has also been applied to the naphthylamines, but in their case the character of the intermediate compound is not nearly so well known as in the case of the naphthols. As Woroshtzow says, (loc. cit.) "One only knows that by the action of bisulphite the naphthylamines are transformed into naphthols with the formation of intermediate bisulphite addition products".

This idea of the naphthols reacting in a tautomeric form has lead to a considerable volume of work being done, not only on the naphthols, which had been investigated by Woroshtzow, but on the phenols, by Fuchs, who had arrived at the same conclusions with regard to the naphthols, namely, that they must react in an additive manner, in the Bucherer reaction, as had Woroshtzow. Fuchs (loc. cit.). Fuchs and Niszel (Ber. 1927, 60, 209) have also applied the idea to the study of the reaction whereby carbazoles are formed by the action of β-naphthol and phenylhydrazine, and they find that it has helped considerably in the study of this complicated reaction. Of more interest however, is the work of Fuchs, and Fuchs

and/

and Elsner, on the bisulphite compounds formed by di and tri- hydroxy phenols. In the case of resorcinol (which had already been studied by Bucherer (loc.cit.), but without very much in the way of positive results) Fuchs and Elsner (Ber. 1920, 53, 886.) find that with boiling sodium bisulphite a compound is obtained which appears to be the sodium bisulphite compound of 3:5 diketohexamethylene 1 sulphonic acid.



3:5 diketohexamethylene 1 sulphonic acid. sodium bisulphite compound.

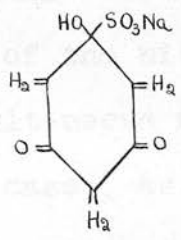
This is what might be expected, if the phenols, which have their double bonds stabilised according to the Woroshtzow theory, react with bisulphite, i.e. for each hydroxyl group there ought to be one molecule of sodium bisulphite added, without the loss of a molecule of water quite apart from any others which may attach themselves to the ring directly. The added molecules of sodium bisulphite have a varying stability,

one/

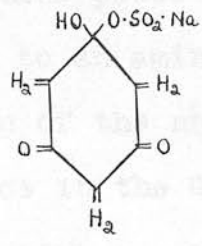
one is lost even in aqueous solution which does not contain free sodium bisulphite, while the last is lost only on boiling. The third and last molecule of added bisulphite, by reason of its stability, must be attached to the ring in a different way to the other two. This disposes of any difficulty there might be in reconciling the addition of three molecules of sodium bisulphite to a dihydroxy phenol, as, using Woroshtzow's theory of addition, the bisulphite should add itself in the same way to each hydroxy group. Hydroquinone was found to behave in a somewhat similar manner (Ber. 1919, 52, 2281) giving 1:4 dihydroxy hexamethylene 1:2:4 trisulphonic acid. Pyrogallol and hydroxy_hydroquinone were also examined (Ber, 1924, 57, 1225). The results in the case of these two latter compounds were similar, in that, they only add on two molecules of sodium bisulphite instead of three, as might be expected from the number of hydroxy groups. In fact only one hydroxy group is enolised, and adds a bisulphite molecule, the other molecule simply goes into the ring as a sulphonic group, as in the case of resorcinol and hydroquinone mentioned above.

The reaction of phloroglucinol was examined with special interest, (Fuchs, Ber. 1921, 54, 245.) because it is well known that phloroglucinol reacts both as a trihydroxyphenol and as triketo_hexamethylene. It/

It was found to unite slowly with sodium bisulphite when heated in aqueous solution on the water bath, to give a mono-bisulphite derivative. Unfortunately, although Fuchs finds evidence for the formation of compounds with more than one molecule of sodium bisulphite, sufficient phloroglucinol was not available for the isolation of these, so that the only compound he obtained was the mono derivative. The exact formula for this is even doubtful. The added group shows the properties of a true sulphonic group in being very stable towards alkalies, but this is somewhat discounted by the fact that a considerable portion of the added sulphur dioxide is eliminated as barium sulphate when the compound is treated with neutral barium chloride solution in the presence of hydrogen peroxide. The graphic formula may therefore be either of those shown below, the only difference being in the attachment of the sulphur atom to the ring, the 1st showing a sulphonic linkage and the 2nd a sulphite linkage.



(1)



(2)

It may be of some interest to note that Bucherer (Ber. 1920, 53, 1457) does not agree at all with these "ketonised" hydroxy compounds. His attack is directed in particular against Fuchs work on resorcinol but he would probably extend it to all similar compounds.

This constitutes a summary of the work done on amino and hydroxy compounds, and their behaviour towards sodium bisulphite, and it now remains to consider the action of bisulphites on nitroso compounds.

The nitroso phenols were apparently first investigated in this respect by Schmidt (J. pr. Ch. 1891, 44, 513) his investigation extending to nitroso phenol, nitroso resorcinol, dinitroso orcinol, nitroso thymol and also to the naphthols. There is also a patent by Geigy & Co.(D.R.P., 71,368, 1894) which deals with the action of sodium bisulphite on nitroso phenol. Dürrwanger (Inaugural Address Munich, 1912) has also investigated the action of sulphites and bisulphites on such compounds as, p-nitroso diphenylamine and nitroso dimethylanaline. In all these cases the fundamental reactions which take place are the reduction of the nitroso group to an amino group, and the simultaneous sulphonation of the nucleus. In some cases, as for instance in the Geigy patent, a side reaction takes place which results in the production of disulphonic acids. A noticeable feature

of/

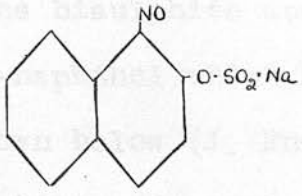
of the work which has been done on the nitroso phenols, and indeed this applies to the nitroso naphthols also, is what might be termed the routine nature of the work. One nitroso compound after another has been treated with sodium bisulphite and the products of the reaction ascertained, wherever possible. There has been apparently no serious attempt to examine the reactions closely in order to ascertain, for instance, if there are any intermediate products, as in the case of the hydroxy bisulphite compounds.

The nitroso naphthols were investigated by Schmidt (loc. cit.) and by Boniger, more fully, three years later (Ber. 1894, 27, 23). They react in essentially the same way as with the nitroso phenols. To take one or two examples, 1 nitroso 2 naphthol 6 sulphonic acid gives, on dissolving in sodium bisulphite solution and treating with dilute acid, 1 amino 2 naphthol 4:6 disulphonic acid while with similar treatment 1 nitroso 2 naphthol 7 sulphonic acid gives 1 amino 2 naphthol 4,7 disulphonic acid.

Of all nitroso naphthols however, perhaps the most interesting both from a theoretical and practical standpoint is 1 nitroso β-naphthol. Theoretically, it is of interest because it forms a bisulphite addition product which can be isolated in a pure state, and can therefore be investigated for structural details/

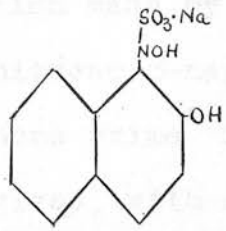
details. Similar compounds are either unknown in the case of the other nitroso naphthols and phenols or are too unstable to be suitable material for investigation. On the practical side it is of interest because, when treated in the manner already indicated i.e. with sodium bisulphite and dilute acid, it gives the important 1 amino 2 naphthol 4 sulphonic acid, while in addition to this the bisulphite compound itself is used in the production of a green mordant dye, but this will be dealt with later.

Although this bisulphite compound has been known for a comparatively long time (since 1891, Schmidt loc. cit.) its constitution was wrongly represented, till recently, when Woroshtzow investigated it (Ber. 1929, 62, 68.) The source of the error may be traced to Bucherer who, as has been said, regarded all bisulphite compounds to be of the nature of esters. The bisulphite compound of nitroso β-naphthol would, on his theory, therefore, be represented by the formula shown below

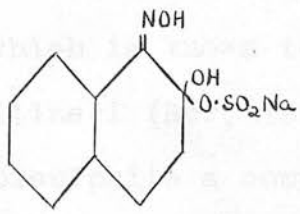


On the Woroshtzow theory of bisulphite compound formation this appeared improbable, and the matter was settled for this particular case by an analysis of/

of the compound by Worostzow, who found a molecule more of water than the above formula contains. There are still two other formulae which are possible even when the one shown above is ruled out, these are



I.

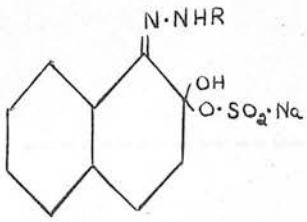


II.

Both of these conform to the results of Woroshtzow's analysis, the difference lying in the position of the added sodium bisulphite molecule.

Formula I is that which has been favoured up till the time of the paper published by Woroshtzow in 1929 (loc. cit.), see for instance Dye Chemistry - Fierz David pp.50.

Woroshtzow, however, draws attention to the analogy in the behaviour of this bisulphite compound with that of the bisulphite compounds of the azo dyes derived from β-naphthol which he has shown to possess the formula shown below (J. Russ. Phys. Chem. Soc., 1911, 43, 771; 1915, 47, 1669, Annales de Chimie 1916, 6, 386)



This is not a true azo form but a quinone hydrazone type of formula.

Another significant fact in determining the correct formula for the bisulphite compound is the observation made by Woroshtzow (loc. cit.), that methyl nitroso β-naphthol which is known to possess the quinone oxime form, Illinski (Ber. 1884, 17, 2584), gives, with sodium bisulphite a compound exactly similar to that given by the unmethylated nitroso β-naphthol. Bearing in mind the type of addition product to expect from a compound of this type (i.e. possessing a ketonic group), we have a useful hint as to which formula, I or II, is the correct one.

Extending these facts to the bisulphite compound of nitroso β-naphthol therefore, formula II appears, on the best evidence at present available to be the correct formula, and it will be the one used in the present work.

This constitutes a survey of the principal reactions of sodium bisulphite in organic chemistry, and particularly with aromatic compounds. The last compound mentioned is, of course, the one which is of particular interest on the present occasion.

OBJECT OF THE RESEARCH.

It can be seen from what has been said regarding the work done on the sodium bisulphite compound of nitroso β-naphthol (and indeed, as has been said, this remark might be applied to many other nitroso compounds) that it still leaves scope for closer scrutiny. The course of the reactions and the nature of the products formed are, in most cases, merely speculations, without experimental evidence to back them up. It is not then surprising to find that the production of the bisulphite compound of nitroso β-naphthol is not quite such a simple process as it appears to be.

It has been found in fact, that when this process is carried out on the large scale the yield of the bisulphite compound varies very considerably. The yield may vary between the wide limits of, nearly theoretical, to absolutely zero. It need hardly be said that this may be a serious matter as the bisulphite compound is used in the production of a green dye. For the production of this dye the bisulphite compound is treated with a ferrous salt in the presence of caustic soda, the iron salt being the mordant of course. Under these conditions the iron salt of nitroso/

nitroso β-naphthol, which is bright green in colour, is produced. This iron salt is known under various names such as, Fast Printing Green (K); Solid Steam Green (F.T.M.); Alsace Green. N. etc. The sodium bisulphite compound itself, is known as Sulphamine (W.D.C.) and Naphthine S (P).

The question of the varying yields of the bisulphite compound constitutes the starting point of this research, and it was hoped that by examining the conditions of its formation, some further information might be obtained about the formation and reactions of one of the few nitroso sodium bisulphite compounds which is available for investigation, in addition to the more practical side of the question, which is the determination of the conditions which will give a good yield of the compound.

METHODS ADOPTED.

In the first place it must be emphasised that the research was on a purely practical problem. That is to say, a certain process used in the manufacture of the sodium bisulphite compound of nitroso β-naphthol was examined step by step exactly as it stood without any thought of forming a theory until a few solid facts could be obtained. No aid could be/

be expected, in any case, from the theoretical side, for there has been, as has been shown,no work done along these lines other than that by Woroshtzow in 1929 (loc. cit) and his results appeared after the essential points in this work had already been determined.

In any case Woroshtzow's work, which is the only one which can be considered as other than superficial, quite misses the important point that it is quite possible to obtain no sodium bisulphite compound when nitroso /3-naphthol is treated with sodium bisulphite.

The first part of this thesis therefore, is a systematic effort to standardise the conditions of this particular process, and trial and error, the only possible method, is the method adopted. It might also be pointed out that in the absence of a working hypothesis or theory (which was the case here) a negative result is of quite as much value as a positive result. Looking back on this particular piece of work it is felt even now, when the answer is known, that any other methods than those adopted would not have given the same insight into the process, as a whole. Any short cuts would have been fatal. If an instance is needed, it is onlynecessary to consider the points which would have been missed if the purified sodium bisulphite product had been used as a starting material instead of examining the actual formation of this material/

material. In this particular work, the initial stages were quite as important as, and were far more difficult to carry out, than the later parts, involving, as they did, a technique for which no precedent could be found.

When the work was started the only certain fact which was known was that in some cases the bisulphite compound could be salted out and in some cases it could not, and in the first stages at least, all the work done was directed towards obtaining absolute constancy in this process of salting out.

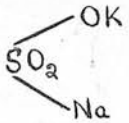
Later on, the salting out time, as it will be called, is used to measure the quantity of a particular form of bisulphite compound present. This measurement of the time taken to salt out appears to be a new quantitative method of analysis. There appears to be no reason why it should not be applied as a method for estimating all compounds which can be salted out. In these experiments it is apparently accurate to 1% if suitable conditions are chosen.

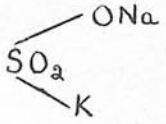
The next sections deal with the constitution of the new sodium bisulphite compound, that is to say, an attempt is made to determine the number and position of the added sodium bisulphite molecules. In this case again (at least in determining the number of molecules added) a somewhat novel method had to be adopted, not from choice, but simply because the stereotyped/

stereotyped methods of organic chemistry were not available.

Finally, some points in connection with nitroso β-naphthol itself, are dealt with, and a theory as to the structure of this compound is put forward, in the Discussion of Results.

One point, which may be disposed of before entering on the experimental part, is the question of two forms of sodium bisulphite. Schwicker (Ber. 1889, 22, 1728) and Barth (Zeit. phys. Ch. 1892, 9, 176) claim to have isolated two different sulphites having the forms





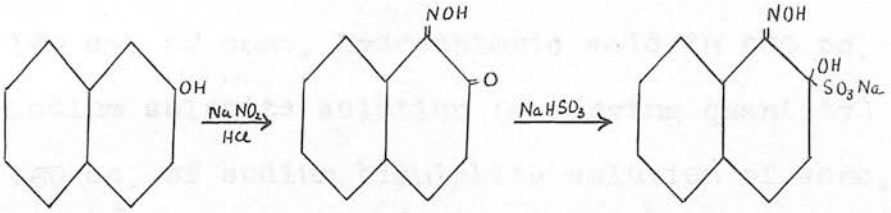
by neutralising potassium bisulphite with sodium carbonate and vice versâ, but there is now overwhelming evidence against their existence. (Röhrig J. pr. Chem. 1888, (2), 37, 217; Fraps J.A.C.S. 1900, 23 202; Godby Proc. Chem. Soc. 1907, 241; Arbusoff J. Russ. Phys. Chem. Soc. 1909, 41, 447; Wright J.C.S. 1914, 105, 2907.)

This point (the only one which has some bearing on the present problem, and of which the published results are convincing enough to be taken for granted) having been disposed of, the experimental part may now be considered.

EXPERIMENTAL.

Preparation of Nitroso β-Naphthol Sodium Bisulphite Compound.

Outline of Method.



Two methods for preparing nitroso β-Naphthol are used:- (1) Henriques, (Ber. 1885, 18, 704;) (2) Stenhouse & Groves (J.C.S. 1877, 1, 47.) The former method, which consists in adding sodium nitrite to a solution of β-naphthol in alcohol, in the presence of zinc chloride, whereby the zinc salt of nitroso β-naphthol is formed and this can easily be converted into nitroso β-naphthol, is not used on the works scale; the method of Stenhouse and Groves is the one which is used and is that indicated in the outline. The detailed account given below is of the method referred to in the introduction as commonly used on the large scale and is of course the one in which the difficulty was encountered. It will be seen/

seen that it is essentially the Stenhouse and Groves method.

The quantities used in the initial experiments were as follows:-

60 gms. β-naphthol .42 mols.

20 gms. of caustic soda in 200 cc. water .50 mols.

35 gms. sodium nitrite in 70 cc. water .50 mols.

140 cc. of conc. hydrochloric acid in 250 cc. water.

Sodium sulphite solution (a varying quantity)

160 cc. of sodium bisulphite solution of conc. 510 gms/litre .43 mols.

160 gms of salt.

The β-naphthol was dissolved in the sodium hydroxide solution and the sodium nitrite solution was added and the liquid cooled to 0°. The hydrochloric acid was then added during the course of an hour. The stirrer used had a hollow centre so that the acid was added under the surface of the liquid. By doing this it was found that the tendency to tar which was present when the acid was merely dropped on the surface was prevented. The addition of acid was continued till the solution was distinctly acid to Congo paper (Fierz-David, Dye Chemistry pp. 50).

The β-naphthol was now almost completely converted into nitroso β-naphthol which was in the form of a bright yellow solid suspended in the liquid in/

in the beaker. This was allowed to stand for 10-12 hours in order to complete the nitrosation.

Formation of the Sodium Bisulphite Compound.

The liquid in which the nitroso β-naphthol was suspended was neutralised by means of sodium sulphite solution and when this neutrality was attained, as indicated by Congo paper, the solution which had been warmed to 20°C. had the sodium bisulphite solution added to it. In about five minutes time if this stage of the reaction was going to proceed normally the nitroso β-naphthol began to lose its intense yellow colour and rapidly became brown, the liquid becoming at the same time much less viscous due to nitroso β-naphthol going into solution. The stirring was continued for an hour, by which time there was not the faintest trace of yellow solid material discernable. The liquid was then filtered to remove a small quantity of tarry matter, the filtrate was clear and varied in colour from pale yellow to deep red.

The volume of the filtrate, in this case about 800 cc., was roughly estimated and salt added at the rate of 20 gms/100 cc. filtrate.

The filtrate containing the salt was now stirred vigorously/

vigorously till all the salt had dissolved. About 10 minutes after this, if the reaction was a normal one, salting out would begin. The liquid became rapidly white in colour due to the separation of the nitroso β-naphthol sodium bisulphite compound. It may eventually become so thick that stirring is difficult.

After standing for an hour the bisulphite compound was separated by filtering and if it was desired, the iron salt could be made by dissolving the bisulphite compound in water, in which it was easily soluble, and adding the calculated quantity of ferrous sulphate and then caustic soda. This latter stage was hardly ever entered upon in the present research however, because it was not at this point that the process broke down.

This method of preparation differs in the following respects from that given by Fierz-David (ibid).

1. The nitroso β-naphthol was not removed by filtration from the liquor from which it was precipitated. This necessitated the removal of the surplus acid by means of sodium sulphite in order to prevent the decomposition of the sodium bisulphite solution which was added in order to form the bisulphite compound. Sodium sulphite was used of course in preference to other salts because the bisulphite formed can be used in the subsequent/

subsequent reaction of formation of the nitroso β-naphthol bisulphite compound.

2. The temperature at which the nitroso β naphthol was dissolved in the sodium bisulphite solution was 20° instead of 5°. This was done in order to save time which may be inconveniently long at 5° under certain circumstances. (pp 88.)

This method remained in outline the method used in all the experiments which follow. Any important changes which were introduced will be fully dealt with as they occur.

Non Salting Out Solutions.

Further quantities of the solution of the bisulphite compound were made according to the directions already given and these showed varying yields, in several cases the solution giving no bisulphite compound at all on the addition of salt.

It was realised that the whole process would have to be rigidly standardised before progress could be made.

Standardisation of the Process.

The standardisation of the process involved more than that any given preparation of a solution of/

of the bisulphite compound would salt out. It was assumed that the variation both in the time which a solution took to salt out and in the yield, was directly proportional to the quantity of the bisulphite compound dissolved in a given volume of water. Therefore, the time which any given solution took to salt out was a direct measure of the concentration of the bisulphite compound present. The following table shows that this assumption is correct.

TABLE I.

In each case 25 cc. of water taken.

No. of Expt.	Weight of compound dissolved.	Time taken to Salt out.*
1	2 gms.	1 min.
2	1.4 gms.	1.5 min.
3	1 gm.	2.5 min.
4	.75 gm.	9 min.
5	.7 gm.	18 min.
6	.65 gm.	No Salting out.

* This is the time from the addition of the salt to the stirred solution containing the bisulphite compound till the solution becomes opaque due to the separation of the bisulphite compound. This time is easy to judge accurately as once salting out sets in the solution becomes very rapidly white. Often the change from faint opalescence to complete whiteness takes place in 5 secs.

This represented the degree of control which was desirable. The ability to produce a solution of the bisulphite compound which would salt out in an absolutely definite time.

The methods adopted to bring this about will now be given. Three different series of experiments were carried out before the process was absolutely under control. These will now be described.

(1) Standardisation of Materials Used.

The following materials were used and the methods used to test their purity and strength are also given. These solutions were used in all subsequent preparations of the bisulphite compound except where otherwise noted.

Hydrochloric acid.

500 cc. of A.R. hydrochloric acid were diluted with 1500 cc. of distilled water. This was standardised against calc spar and found to be 3.912 N. Subsequent lots of acid were made up to this strength.

Sodium hydroxide.

A.R. sodium hydroxide was used. 110 gms. were dissolved in a litre of water and six litres of this solution made up at a time. It was found to be 1.237 N. This figure was checked every month.

Sodium/

Sodium nitrite.

The ordinary B.D.H. sodium nitrite was recrystallised and dried. 125 gms. of this ± .01 gm. was weighed out, dissolved in distilled water and the solution made up to 250 cc. This solution was not standardised by any of the recognised methods such as by potassium permanganate, but by a method which was more useful for the purpose to which it was being put in these experiments. As the reaction which the sodium nitrite undergoes in the process is decomposition by hydrochloric acid it was decided to standardise it against the acid. This was done by titrating 5 cc. of the sodium nitrite solution (at the boiling point in order to expel nitric oxide formed) with the hydrochloric acid. The end point was determined by spotting on Congo Red paper. This method gave remarkably consistent results, three estimations being within ± .02 cc. It was found that 5 cc. of nitrite solution were equivalent to 7.22 cc. of acid.

Sodium sulphite solution.

This was used to remove the excess of acid used in the preparation of the nitroso β-naphthol, before the addition of the sodium bisulphite solution. It was made up by dissolving 20 gms ± .01 gm. of crystalline sodium sulphite in 100 cc. of distilled water.

Sodium/

Sodium bisulphite solution.

This was made up by dissolving 420 gms. of sodium metabisulphite in a litre of distilled water and filtering. The accurate standardisation of this solution by means of alkali is not easy because of the poor end point (Scott, Standard Methods of Chemical Analysis 1917, pp.411). After several attempts to use this method of standardisation it was given up and the metabisulphite was weighed out correct to ± .1 gm. This appeared to be a perfectly satisfactory method.

β -naphthol.

B.D.H. resublimed β -naphthol was used. This was found to be free from α -naphthol by the bleaching powder test and also passed the tests given in the B.D.H. book of A.R. standards.

(2) Repetition of the Process with Standard Reagents.

For these experiments the quantities used were reduced somewhat. The β -naphthol was weighed out correct to ± .05 gm. and the other solutions were added. The accuracy being probably of the order of ± 1 cc.; about that usually attained in organic preparations on this scale.

The/

The quantities used were:-

β-naphthol	14.4 gms.
sodium hydroxide solution	81 cc.
sodium nitrite solution	18 cc.
hydrochloric acid	60 cc.
sodium sulphite solution	depending on the acidity, as shown by Congo Red paper.
sodium bisulphite solution	38 cc.
Water	200 cc.

The results were only moderately successful. The sodium bisulphite compound was now produced with fair regularity but the time which it took to salt out was very far from being constant. The following table shows this.

TABLE 2.

No. of Expt.	Time to Salt Out.
1	40 mins.
2	20 mins.
3	1 hr. 45 mins.
4	60 mins.
5	45 mins.

(3) Complete Standardisation.

The change introduced was the use of burettes and pipettes for measuring all solutions, this ensured an/

an accuracy of ± .01 cc. In addition the end point as shown by Congo Red paper was very carefully determined. Otherwise the process was carried out exactly as before. The results obtained were entirely satisfactory. The salting out time figures for three consecutive preparations were:-

(1) 23 mins.

(2) 23 mins.

(3) 24 mins.

Having obtained the necessary degree of control of the process it was now possible to examine the effects obtained by altering the process. It was apparent that this could be done in four ways (a) altering the quantity of sodium nitrite (b) altering the volume of the solution (c) altering the quantity of acid in the preparation (d) altering the quantity of sodium bisulphite.

An examination of these factors was carried out.

Effect of Varying the Quantities of Substances used in the Preparation of the Sodium Bisulphite Compound.

(a) A shortage of sodium nitrite might have at least two effects (1) a diminution in the quantity of nitroso β-naphthol produced or (2) the formation of a compound of intermediate composition between β-naphthol/

β-naphthol and nitroso β-naphthol. Each of these might be the cause of irregular salting out.

Quantities of sodium nitrite between .5 and 1.5 times the theoretical quantity needed to convert all the β-naphthol into nitroso β-naphthol were used. The volume of acid used was carefully adjusted to allow for the varying quantities of nitrite, the rest of the process remained unchanged.

The salting out times showed no relation to the amount of sodium nitrite used except a lengthening of the time as soon as the quantity of nitrite fell below the theoretical quantity. If this was caused simply by a fall in the concentration of nitroso β-naphthol sodium bisulphite compound brought about by the presence of a certain amount of unnitrosated β-naphthol then the same effect would be obtained and could be examined more conveniently under (b). Alteration (b) was examined therefore.

(b) The solutions of the bisulphite compound were made exactly as before, pp. 32. To these solutions were added varying quantities of water as shown below.

TABLE 3.

No. of solution.	cc. of water added	Time to Salt out.
1	0	23 mins.
2	25	39 mins.
3	50	57 mins.
4	100	80 mins.

These figures showed that the time taken to salt out depended directly on the concentration of the bisulphite compound, and explained the effect obtained under (a). This fundamental fact had of course already been verified in another way (pp.28).

(c) In examining the effect of alteration in the quantity of acid used in the preparation, it must be noted that there are two points in the process at which it can play a part.

(1) by acting directly on the nitroso β-naphthol during the 10-12 hours while the nitrosation is being completed.

(2) by decomposing the sodium sulphite used to neutralise the excess of acid, this would be equivalent to the addition of an excess of sodium bisulphite.

No.1 was investigated first.

Effect of Acid (1).

A preparation was made as indicated on pp.32 (the volume of added water however was reduced from 200 cc. to 100 cc. which accounts for the reduction in salting out time from 23 mins. to 6 mins.) and portions were removed in a 25 cc. pipette after varying times. To each of these 25 cc. portions 2.5 cc. of sulphite solution were added to remove the excess of free acid, and then 5 cc. of bisulphite solution; they/

they were then stirred for 30 mins., filtered, and 10 gms. of salt added.

The results of this experiment were:-

TABLE 4.

No. of Sample	Time of standing in acid solution.	Time to salt out.
1	7 hrs.	6 mins.
2	18 hrs.	8 mins.
3	42 hrs.	18 mins.
4	142 hrs.	no salting out.

The effect of the acid is noticeable but the magnitude of the effect is not nearly great enough to account for the ordinary type of non salting out as in the ordinary course of events the nitroso β-naphthol is never allowed to stand in presence of acid for more than 12 hours.

Expt. 2.

This next experiment was carried out to see if a similar increase took place when the nitroso β-naphthol was allowed to stand in neutral solution. The usual preparation of nitroso β-naphthol was made but after standing in acid solution for 12 hours dilute sodium hydroxide was added very carefully to the suspension till it appeared to be neutral, as shown by litmus (the litmus end point lies nearer true neutrality than the other indicators commonly used/

used; Rosolic acid was tried but was found not so good as litmus).

The results were:-

TABLE 5.

No. of sample.	No. of hours between neutralisation and addition of $NaHSO_3$	Time to salt out.
1	4 hrs.	6 mins.
2	66 hrs.	10 mins.
3	90 hrs.	10.5 mins.
4	138 hrs.	5 mins.
5	234 hrs.	6.5 mins.

Finally the effect of standing in alkaline solution was tried.

These results were what was expected. No change in the nitroso β-naphthol was anticipated under these conditions.

Expt. 3.

This series was completed by allowing the nitroso β-naphthol to stand in alkaline solution.

In the first place it should be noted that the concentration of hydroxyl ions can never be very great because nitroso β-naphthol dissolves in sodium hydroxide solution to give its sodium salt so there is no point in adding sodium hydroxide after the first appearance of the green sodium salt colour.

The/

The results were:-

TABLE 6.

No. of Sample.	No. of hours between addition of NaOH and addition of $NaHSO_3$	Time to salt out.
1	7 hrs.	7 mins.
2	23 hrs.	10 mins.
3	119 hrs.	16 mins.

This result was of course totally unexpected as it was thought that if the effect of acid was to prolong the time of salting out the effect of an alkaline solution would not be the same. An explanation of this effect is attempted in the Discussion of Results.

Effect of Acid (2).

As has been pointed out the acid used in the preparation of the nitroso /3 naphthol might have another action. In those preparations which had variable salting out times the quantity of acid added was rather indefinite and also this acid was always neutralised by sodium sulphite. It was evident that this was equivalent to the addition of varying quantities of sodium bisulphite. That is to say there appeared a possibility that non salting out was due to an excess of sodium bisulphite.

It/

It seemed that the simplest way to test this hypothesis would be to add varying quantities of sodium bisulphite to a fixed weight of dry nitroso β-naphthol. The reason for using dry nitroso β-naphthol had better perhaps be explained.

The only really reliable solution upon which this experiment could be performed were those whose salting out time was constant, now as has been shown there was up to date only one method of obtaining such a solution (see pp. 33) and this involved a separate preparation for each experiment which was a very slow and tedious method. A much better method appeared to be the preparation of a large bulk of nitroso β-naphthol from which accurately weighed samples could be taken.

This was done, the nitroso β-naphthol was carefully washed till free from chloride and acid, and dried without artificial heat or the presence of drying agents. The reason for this will be found in the section dealing with nitroso β-naphthol (pp.93). The quantities used were:-

nitroso β-naphthol	2.600 gms.
distilled water	40.0 cc.
sodium bisulphite solution	5.0 cc.

This was stirred in a large test tube in a bath at 20° for 30 mins. during which time a further addition of sodium bisulphite solution or water, making a total volume/

volume of 3 cc. was made. The solution was removed, filtered, transferred to the bath again and 20.0 gms. of salt added.

The results were:-

TABLE 7.

No. of Expt.	ccs. $NaHSO_3$ added in excess to the standard 5 cc.	ccs. water added.	Time to salt out.
1	0	5	28 min.
2	1	4	60 min.
3	2	3	no salting out

It was decided to check the experiment by repeating No. 1.

The result was:-

Time to Salt Out 65 min.

This result showed that this method of examining the effect of sodium bisulphite in preventing salting out would have to be abandoned as the nitroso β-naphthol was changing while the experiments were being carried out. This was traced to the action of light and was so difficult to obviate that the method had to be abandoned. The whole matter is discussed more fully in the section on nitroso β-naphthol. (pp. 103)

A New Method for Investigation of the Action of Bisulphite.

In view of the above results the only course seemed to be to make separate preparations of nitroso β-naphthol and add to each varying quantities of sodium bisulphite solution. As there seemed to be some prospect of having to make a large number of these it was decided to cut down the quantities considerably. This involved of course, the possibility of error to a larger extent than before. For instance, there was nearly always formed during the preparation of the nitroso β-naphthol a small quantity of tar, while this may have no effect on a large scale preparation it may easily effect a considerable reduction in the quantity of nitroso β-naphthol available for reaction with the sodium bisulphite in a small scale preparation. Accordingly in these experiments the preparation of nitroso β-naphthol was carried out in an atmosphere of nitrogen which prevented to a large extent the formation of any of the surface oxidation products, which constitute the tar.

The quantities used were:-

β-naphthol	2.500 gms.
Sodium hydroxide soln.	17.00 cc.
Sodium nitrite soln.	3.00 cc.

Hydrochloric/

Hydrochloric acid	11.35 cc.	
water (1)	20.00 cc.	
Sodium sulphite soln.	5.00 cc.	
Sodium bisulphite soln.	5.00 → 10.00 cc.	Total of these two always 10.00 cc.
water (2)	0. ← 5.00 cc.	
Total volume	66.35 cc.	
Salt for Salting out	25.00 gms.	

Assuming that 5 cc. of sodium bisulphite solution are used and making no allowance for the amount of bisulphite which was formed by the decomposition of the sulphite (which was very small) it will be seen that approximately 2 mols. of sodium bisulphite were being used to dissolve 1.7 mols of nitroso β-naphthol.

Water (2) was used to maintain the volume constant when the sodium bisulphite is varied. The other quantity of water (1) was used for washing purposes.

A very rigid procedure was adopted in the making of these separate preparations to insure as far as possible uniform quality throughout the series. The main points were that (1) the nitroso β-naphthol after formation was allowed to stand for 22 hours at a constant temperature 12°-13° in an atmosphere of nitrogen. (2) the bisulphite solution was stirred for exactly 30 minutes at $20^{\circ} \pm 1^{\circ}$. (3) the salting out was carried out at $20^{\circ} \pm 1^{\circ}$

The/

The results obtained were:-

TABLE 8.

No. of Expt.	Total ccs. $NaHSO_3$ solution added.	Time to Salt Out.
1	5	7 mins.
2	6	18 mins.
3	7	40.5 mins.
4	8	no salting out.

It will be seen from these results that the non salting out of the bisulphite compound was due to the presence of an excess of sodium bisulphite.

If the effect of adding an excess of acid and then neutralising with sodium sulphite is investigated from this standpoint it will be seen that using solutions of the concentrations given on pps. 29-31 which were those used, 3.1 cc. of acid would have the same effect as 3.0 cc. of sodium bisulphite.

It is now unnecessary to examine factor (d) mentioned on pp.33 as the experiments resulting from examining the effect of acid have solved this problem.

The Effect of Sodium Bisulphite on a Solution of the Sodium Bisulphite Compound.

A method by which a large number of experiments on the action of sodium bisulphite could be made in

a/

a reasonable time now became necessary if any considerable progress was to be made in investigating this interaction between nitroso β-naphthol and sodium bisulphite.

The ideal method would be to make a large volume of the bisulphite compound solution and take portions of this and add varying quantities of sodium bisulphite to them. If this could be done it would be unnecessary to make a separate preparation of nitroso β-naphthol for each experiment with the sodium bisulphite solution and there would be an enormous saving in time, but there were two difficulties in the way of doing this:-

(1) the salting out time of such a bisulphite compound solution does not remain constant.

(2) the bisulphite solution decomposes on standing, giving 1 amino 2 naphthol 4 sulphonic acid.

Difficulty No.1 is perhaps best explained as follows.

It was found that if one of these non-salting out solutions (A solution was taken to be incapable of salting out at this stage in the work when after stirring for 3 hrs. no signs of a ppt. was obtained. This was purely arbitrary but in fact it was later found that in no case did a solution salt out after 2 hrs. stirring. However this matter will be dealt with more fully later) was taken, divided into two equal/

equal portions and salt added to one half, no salting out was obtained of course. On allowing the other half to stand exposed in an open beaker for varying times as shown below (Table 9) the bisulphite compound could be salted out.

TABLE 9.

No. and division of Prep.	Time from Addition of $NaHSO_3$ to addition of Salt.	Time to Salt Out.
(1) 1st half	55 mins.	No salting out.
(1) 2nd half	6 hr. 10 mins.	1 hr. 30 min.
(2) 1st half	59 min.	No salting out.
(2) 2nd half	6 hr. 5 min.	55 mins.
(3) 1st half	1 hr. 7 min.	No salting out
(3) 2nd half	6 hr. 19 min.	1 hr. 20 min.

These solutions showed therefore on standing an increase in ability to salt out. It ought to follow that those preparations which salt out but give only very poor yields (as is the case with some) ought to give better yields when allowed to stand for some time before the addition of salt. This was found to be the case. (Table 10)

TABLE 10./

TABLE 10.

No. and division of prep.	Time from addition of $NaHSO_3$ to addition of salt.	Time to salt out	Yield.
1) 1st half	50 mins.	20 mins.	poor yield.
2nd half	24½ hrs.	10 mins.	very good yield.
2) 1st half	56 mins.	45 mins.	very poor yield.
2nd half	45 hrs.	12 mins.	very good yield.

It will be seen from these results that a solution of the bisulphite compound could not be allowed to stand by itself and remain constant with respect to its salting out time, a necessary condition for these experiments.

The cause of this change cannot be conveniently discussed here as there are other facts bearing on it which can only be introduced later. The whole matter is therefore left over to the discussion of results. (pp. 108).

With regard to (2) it was early noted during the preparation of these solutions that after a variable number of days or in some cases hours, fine needle-shaped crystals were deposited. On separating these they were found to be 1 amino 2 naphthol 4 sulphonic acid. A consideration of the probable cause of this, however, led to the elimination of this undesirable factor/

factor in the following way. As 1: 2: 4 acid is produced by the action of acid on the sodium bisulphite compound of nitroso β-naphthol in presence of excess of Sodium bisulphite, it followed that the solution of the bisulphite compound must be acid if 1: 2: 4 acid was formed. The only cause of this could be the acidity introduced by the sodium bisulphite solution and this was actually found to be the case.

A bisulphite compound solution was prepared from sodium bisulphite solution from which nearly all the sulphur dioxide had been removed at the pump. This solution was kept for a week and there was no trace of 1: 2: 4 acid , on saturating with Sulphur dioxide however, a heavy precipitation of crystals of 1: 2: 4 acid took place in 24 hours.

When this fact was observed the undesirable factor (2) could be eliminated, and it appeared that (1) might be not so serious as had been supposed if the series of experiments could be run through quickly. Accordingly a solution of the sodium bisulphite compound was made up using the following quantities.

β-naphthol	15.00	gms.
Sodium hydroxide solution	102.0	cc.
Sodium nitrite "	18.00	cc.
Hydrochloric acid "	68.95	cc.
Sodium sulphite "	30.00	cc.

Sodium/

Sodium bisulphite solution (free of Sulphur dioxide) 30.00 cc.

Water 120.0 cc.

This was made in an open beaker, the atmosphere of nitrogen no longer being necessary when these larger quantities were used.

50 cc. portions were taken for each experiment and the volume made up by either $NaHSO_3$ solution or water, or both, to 54.56 cc.

20.0 gms. of salt are added and the salt out carried out at 20°.

Results.

TABLE 11.

No. of Expt.	ccs. $NaHSO_3$ added.	ccs. water.	Time to salt out.
1	0	4.56	5 mins.
2	.91	3.65	11 mins.
3	1.82	2.73	38 mins.
4	2.73	1.82	no salting out.
5 as (1)	0	4.56	5 mins.

The time between Nos.1 and 5 was 4 hrs. so that during this period the solution had not of its own accord changed its salting out time.

Another similar series was also obtained but the numerical values are different as the solution was made up in a different way (using sodium carbonate instead/

instead of sodium sulphite to remove the excess of acid, this will be explained later pp. 53)

TABLE 12.

No. of Expt.	ccs. water	ccs. $NaHSO_3$	Time to Salt Out.
1	2.30	0	5 mins.
2	1.80	.50	9 "
3	1.55	.75	13 "
4	1.45	.85	14 "
5	1.35	.95	21 "
6	1.30	1.00	26 mins.
7	1.20	1.10	no salting out.

Further Examination of the Action of the Sodium Bisulphite Solution; Attempt to make Direct Measurement of pH of a Bisulphite Compound Solution.

Although it had been conclusively shown that the addition of sodium bisulphite solution was unfavourable to, and eventually prevented salting out, the cause of this had not been made clear. The most probable action of the bisulphite solution apart from forming a compound with the nitroso β-naphthol sodium bisulphite compound was its action in raising the pH of the solution. It appeared not altogether improbable that this might be the cause of non salting out due/

due perhaps to the formation of some compound having a composition intermediate between the bisulphite compound and 1 : 2 : 4 acid, which would be expected to be formed in solutions of an acid nature, and which might not salt out. The possibility of this was heightened in view of the work done by Woroshtzow and Kassatkin, (Ber. 1929, 62, 57) in which they show that the sodium bisulphite compound formed by β-naphthol 1 sulphonic acid becomes increasingly unstable with decreasing pH. In this case a reverse of the above would give the necessary conditions for non salting out.

Accordingly, attempts were made to make comparisons between the pH of a solution of the bisulphite compound and its salting out time. This was found to be extremely difficult owing to the very great poisoning effect of the bisulphite compound solution on the electrode. Ordinary platinum electrodes proved quite useless and a quinhydrone electrode could not be used as the quinhydrone dissolved in the bisulphite solution. A glass electrode in conjunction with a Lindeman electrometer would probably have been the best combination but these were not available so an electrode described by Parker (Indust. & Eng. Chem. 1925, 17, 737) consisting of a thick tungsten wire surrounded by Mn_2O_3 was tried. This gave results which, while not satisfactory, yet seemed to show

that/

that the difference of pH's between the solutions which would, and would not, salt out, were of an extremely small order.

These experiments were not in any case pushed very far as another and easier way of finding whether the hydrogen ion concentration of the bisulphite compound solution was connected with its salting out time was discovered. This is described in the next section.

Introduction of Sodium Carbonate in Place of Sodium Sulphite in the Preparation of the Bisulphite Compound Solution.

If it is the action of the sodium bisulphite solution in raising the pH of the bisulphite compound solution which is responsible for non salting out, it ought to follow that anything which raises the pH of the solution should have the same effect. The experiment to be carried out therefore is simply to add the requisite quantity of acid instead of sodium bisulphite solution. It should be noted however that if acid is added to a solution of the bisulphite compound prepared according to the directions on pp. 47, sodium bisulphite is going to be liberated which might mask the action of the acid, therefore it is advisable to substitute sodium carbonate as an acid remover in preparing the bulk solution of the bisulphite/

bisulphite compound. For the sake of comparison and to show that there is a complication when sodium sulphite is used, the experiments performed with the solution free from sulphite were also done with a solution containing sulphite.

In the actual experiments acetic and phosphoric acids as representive organic and inorganic acids were added to a bisulphite compound solution preparation which had been prepared (1) with sulphite (2) with carbonate. (It is inadvisable to use a strong mineral acid like hydrochloric or sulphuric as there is the possibility, in fact the certainty, of decomposing the bisulphite compound solution).

These acetic acid and phosphoric acid solutions were made equal in strength (as determined by titration with caustic soda and phenolphthalein) to the sodium bisulphite solution.

Sodium Sulphite prepared solution.

In all the succeeding experiments the volumes are kept constant.

2.73 ccs. of sodium bisulphite solution required to prevent salting out in this series.

TABLE 13./

TABLE 13.

No. of Expt.	ccs. of acetic acid added.	Salting out time.
1	0	5 min.
2	.91	5 min.
3	1.82	7 min.
4	2.73	10 min.

TABLE 14.

No. of Expt.	ccs. of Phosphoric acid added.	Salting out time.
1	0	5 min.
2	.91	7 min.
3	1.82	7 min.
4	2.73	10 min.

Sodium carbonate prepared solution.

This is the solution referred to on pp.48 . The only difference between this preparation and the preparation of a sulphite prepared solution (see pp. 47) are the introduction of the following quantities.

Sodium carbonate soln. 11.50 cc. instead of sodium sulphite soln. 30 cc.
Sodium bisulphite " 40.00 cc. instead of sodium bisulphite soln. 30 cc.

1.1 cc. of bisulphite solution were necessary to prevent salting out in this series but in order to make very sure that any action which there might be would/

would not be missed 3 cc. of acetic and phosphoric acid were added, that is, approximately three times the quantity of sodium bisulphite which would produce non salting out.

Results.

TABLE 15.

No. of Expt.	ccs. added.	Time to salt out	Duplicate Expt.
1	3 cc. water	4 min.	4.5 min.
2	2 cc. acetic acid	4.5 min.	4.5 min.
3	3 cc. phosphoric acid	4 min.	4 min.

It might be noted that those salting out times which are relatively short (under 10 mins) are liable to vary somewhat more than the longer ones. This is probably due to different rates of saturation of the solution with salt due to the stirrer having slightly different speeds of rotation from one experiment to another.

This experiment gave conclusive proof that it was the addition of an excess of sodium bisulphite above that necessary to form the ordinary bisulphite compound which was responsible for the non salting out, and further, that as the pH of the solution had no effect on salting out, the alternative theory, that a compound is formed between the bisulphite compound and sodium bisulphite is now the one which must/

must be investigated.

Before attempting to isolate this hypothetical compound it is necessary to attempt to get some idea of its properties when in solution, as it appeared that its isolation must be attempted from the solution in which it is readily formed. This involves an investigation of the behaviour of solutions of the bisulphite compound and more particularly of those solutions which do not salt out.

Investigation of the Reactions of a Solution of the Compound formed between Sodium Bisulphite and the Sodium Bisulphite Compound.

Two facts can be deduced about the nature of this compound from the experimental work already done.

(a) it must be very soluble in water.

(b) it must be rather unstable.

Assumption (a) is justified on the grounds that the bisulphite compound which can be readily prepared in a pure state, as will be explained later, is itself readily soluble in water, so that if the conversion of some of it into another compound, in all probability also a sodium salt, prevents salting out, this second compound must be even more soluble.

(b)/

(b) may be seen to be true by considering the figures given on pp. 45 . Evidently the compound is reconverted into the ordinary bisulphite compound at ordinary room temperature if no precautions are taken to protect it.

The best line of action seemed to be to find what conditions were necessary to preserve the compound in its original state, or perhaps more accurately to prevent the reformation of the ordinary bisulphite compound. This of course is equivalent to saying, find the conditions under which a non salting out solution will not recover and salt out.

It was now necessary therefore, to investigate more thoroughly the experiments carried out at an earlier date and whose results are given on pp. 45 .

Those solutions which recovered from non salting out condition were simply allowed to stand in an open beaker exposed to light and air. Taking these conditions into consideration the following seemed to be the most likely causes of this recovery.

(1) Some effect due to light.

(2) Evaporation which would increase the concentration of the solution.

(3) Oxidation by the atmosphere.

(4) Effect of the glass, i.e. reduction of the sodium bisulphite content by the alkali in the glass.

(1), (2) & (4) were easily tested as follows:-

(1) Two samples of the same solution, of salting out time (25 mins), were placed, one in a covered flask, and the other in a flask exposed to light. After 24 hours they were salted out, one salted out in 10 mins. and the other in 11 mins., hence it was concluded that light was not the cause.

(2) Two samples of a solution (same as in (1)) of salting out time 25 mins. were placed in two evaporating dishes. One was left exposed to the air overnight, the other was covered except the spout. Both salted out next day in 11 mins.

(4) In this case the solutions were kept in ordinary soft soda glass flasks and in Jena glass flasks respectively. It would be expected that if the glass had any effect those in the soda glass flasks would show the greatest recovery. The solutions were made up as in (1) and (2) and the results on salting out after 24 hours were Soda glass 9 mins. Jena glass 10 mins.

These three factors can therefore be eliminated.

(3) A roughly carried out experiment in which a non salting out solution was made up and placed in tubes filled with oxygen and hydrogen respectively showed that oxidation was probably the cause of the recovery/

recovery. The salting out times recovered from ∞ to 17 mins. for the hydrogen filled tube and ∞ to 9 mins. for the oxygen filled tube.

It was found extremely difficult in this series of experiments to maintain the solution in a non salting out condition. It must be said however, that this is partially understandable as in no case was a large excess of bisulphite solution added, in most cases just sufficient to prevent salting out. The method eventually used was to fill two tubes 6" x 1" with pure nitrogen, purified by passing the gas from a cylinder over heated copper, and other two boiling tubes with pure hydrogen also obtained from a cylinder. All the air was removed by successively evacuating the tubes at the pump and filling them from reservoirs of hydrogen and nitrogen respectively. This flushing out was repeated four times. The bisulphite compound solution was then made up to be non salting out and quickly run into the tubes by means of tap funnels, the tubes being partially evacuated to assist this. Connection was then again made to the reservoirs of nitrogen and hydrogen and the solutions were left in contact with these gases overnight under slight pressure (about 1 ft. of water). The following morning salt was added to each tube and the solution stirred. This was carried out in an open tube so that the solution/

solution was exposed to the oxygen of the atmosphere. The following results were obtained.

TABLE 16.

Time to Salt Out before putting in tube.	Solutions kept in H_2 atmosphere for 24 hrs.	Solutions kept in N_2 atmosphere for 24 hours.
∞	60 mins.	56 mins.
∞	∞ *	∞ *

A similar solution was left in a loosely stoppered flask overnight and therefore exposed to oxygen.

Salting Out time - 18 mins.

An even more convincing experiment which showed the action of the air on these solutions was carried out as follows.

A non salting out solution was made up and placed in a tube which was closed with a rubber stopper through which passed a stirrer fitted with a mercury seal. In this way the solution was kept in a non oxidising atmosphere by filling the tube with hydrogen.

Salt was added and the solution was stirred for 19 hours but no salting out took place.

The/

* In the expts, marked * the stirring was stopped after 30 mins. as it was suspected that it was the stirring that was causing the salt out. This will be fully explained however under a later section. (pp. 61)

The stirrer was then replaced by an ordinary one so that the solution was now exposed to the air and the stirring continued. Salting out now took place after 3 hours stirring.

It was considered that there was now sufficient evidence to justify the conclusion that the recovery of the bisulphite compound solution from the non salting out condition is due to oxidation.

Further Investigation of the Conditions affecting Salting Out.

There were however three further points which needed investigation. These were:-

(1) (a) how far the actual mechanical stirring assisted salting out and (b) how much is due to oxidation.

(2) the effect in solutions unsaturated and saturated with salt.

(3) the effect of adding sodium hydroxide to a non salting out solution.

(1) (a) This was investigated with the pure bisulphite compound (the preparation of which will be described later) as the effect is much more under control in this case, for, as will be shown, the purified compound has the property of not being affected by the air.

As/

As might be expected the pure bisulphite compound can be salted out when it is dissolved in water in the proper concentration. By choosing the concentration, solutions of any desired salting out time can be prepared and it was with these that the effects of stirring were observed.

By dissolving .70 gms. of the pure bisulphite compound in 25 cc. of water and adding 10 gms. of salt a solution was obtained which showed that the actual mechanical effect of stirring aids salting out. After 18 mins. stirring, the solution became slightly opalescent and on stopping the stirrer small particles of the salted out bisulphite compound could be seen floating about. The solution was allowed to stand for 7 mins. during which no increase in the precipitation took place. On stirring again for 1 minute a very noticeable increase took place which again stopped on stopping the stirrer. In fact the solution could be salted out by stages simply by stopping and starting the stirrer.

(1) (b) On referring to table 16, pp.59 it will be seen that two results are marked with an asterisk and the explanation is given. This alteration between the treatment of the two solutions was made because it was suspected that the stirring was causing the oxidation of the solution and hence the salting out.

This/

This effect is of course especially noticeable in solutions of small bulk so that practically any solution can be made to salt out if the stirring is continued long enough. Besides the two examples already given of this particular action of stirring another even more striking was carried out as follows:-

A solution was made up to be non salting out when stirred in an atmosphere free of oxygen obtained as explained previously (pp. 58) Portions of this solution were then treated in the following manner:-

(a) Stirred in an atmosphere of hydrogen for 19 hours, no salting out.

(b) Stirred for 20 mins. and allowed to stand in air, no salting out after 2 days.

(c) Stirred continuously in air. Salted out after 1 hr. 30 mins.

These results show that in addition to the actual mechanical effect of stirring which has been shown to aid salting out, stirring, in so far that it helps the process of oxidation by the oxygen of the air also helps salting out in this particular case.

A not very well verified but interesting observation was that this recovery from the non salting out state brought about by stirring seems to be more noticeable at temperatures under than over 20°.

These experiments are of course another clear demonstration of the oxidation effect and need not have/

have been included as such, as that effect has been already demonstrated. They serve,however, to emphasise the fact that under the heading of stirring two distinct effects can be obtained.

(2) It had been noticed that in the majority of cases once salt had been added to a solution of the bisulphite compound and salting out had not been effected at the first attempt, the solution showed little power of recovery from its non salting out condition as indicated by salting out on recommencing the stirring after standing exposed to the air.

Two experiments showed that this was actually the case. Both were carried out in the same way. A solution was made up to be non salting out (this is now only a relative term of course and signifies a solution which will not salt out in 30 mins). One half was allowed to stand overnight exposed to the air; the other half had salt added to it and was stirred for 10 mins. in order to saturate the solution and it was also allowed to stand overnight. After standing overnight the 1st half then had salt added and was stirred and the salting out time observed. The stirring of the 2nd half was recommenced and its salting out time observed.

The results were:-

Expt. 1./

Expt. 1.

Sodium bisulphite soln. added 2.2 ccs.

1st half. (no addition of salt)

Salting out time after standing 16 mins.

2nd half. (saturated with salt)

Salting out time after standing 50 mins.

(very poor yield)

Expt. 2.

Sodium bisulphite soln. added 2.4 ccs.

1st half.

Salting out time 20 mins.

2nd half.

Salting out time 1 hr. 30 mins.

(3) The effect obtained on adding sodium hydroxide to a non salting out solution is highly significant as regards the probable constitution of the non salting out compound, as will be shown in the discussion of results. The effect is always the same, the solution salts out a short time after the addition of the alkali. Usually a small quantity of a dilute solution of sodium hydroxide is sufficient. 5 cc. of N. sodium hydroxide is ample for any of the non salting out solutions mentioned in table 16 .

Conclusions Drawn from Experiments on the Solutions of the Bisulphite Compound.

So far all the experiments had been performed on a possibly impure bisulphite compound and certainly on a bisulphite compound in the presence of more than salt and water (the solutions are deeply coloured for instance). It seemed that all the useful information to be extracted by this method of experiment had now been exhausted, and in particular the solutions had shown themselves to be unsuitable for further treatment with a view to isolating the compound formed with excess of bisulphite. It can be seen for instance that it would be necessary to carry out all operations in a non oxidising atmosphere because of the readiness with which the non salting out compound is oxidised to the salting out form in these particular solutions. It was decided therefore, to use the pure dry bisulphite compound itself, for similar experiments, in order to see how far its behaviour differed from that of the bisulphite compound which had never been extracted from solution and purified.

Experiments on the Pure Bisulphite Compound.

This is comparatively easy to prepare. The method given by Woroshtzow (Ber 1929, 62, 68) was used/

used. His method of preparation of the bisulphite compound is exactly the same in outline as that already given (pp. 24-27) except that the nitroso β-naphthol is dissolved in the sodium bisulphite solution at 5° instead of 20°. The salted out product was purified as follows. 100 gms. was dissolved in 400 gms. of water at 25°. To the filtered liquid which was red brown in colour half its volume of alcohol was added. This solution was allowed to stand for 4 hours in ice and was then filtered. The precipitate was washed with 50 cc. of dilute alcohol (1 part alcohol 2 parts water) and then with absolute alcohol. Woroshtzow found it necessary to recrystallise from hot aqueous alcohol to free the crystals from a red-brown colour which they possessed. In this case however, it was found unnecessary to recrystallise from hot alcohol as the precipitate which separated on the addition of alcohol to the aqueous solution of the crude compound was practically pure white after washing with a little alcohol. An analysis of the sodium content showed

Na found	8.10%
" "	8.12%
Na reqd.	8.30%

Its decomposition point was found to be 190°-195°.

It will be remembered that the first purpose of the investigations of the action of sodium bisulphite solution/

solution on the crude bisulphite compound solution (as it will now be called) was with a view to finding the conditions likely to lead to a successful method of isolation of the non salting out compound.

The same policy was pursued in this case so that the 1st experiment was carried out with a view to ascertaining how much the oxidation effect was in evidence. The methods employed were similar to those used before, the only difference was that the solution was not made up to be non salting out but merely to have a long salting out time. It can be seen that this gives more valuable information than a completely negative result.

The quantities used in each case were

1.70 gms. bisulphite compound

50 cc. water.

1.00 cc. of sodium bisulphite solution.

Each was divided into two, and 10 gms salt added when the salt out was begun.

The results were.

TABLE 17.

No. of Expt.	Time to Salt Out on adding Salt immediately.	After standing overnight.
1	45 mins.	60 mins.
2	45 mins.	56 mins.

This/

This result shows that not only does the solution fail to recover from a non salting out condition but the action actually proceeds in the opposite direction. This can be understood, as the time between adding the excess sodium bisulphite and the salt out is only 45 minutes which is probably not sufficient time for all the sodium bisulphite to react. This was confirmed in another way at a later date. (see pp. 83)

The experiment mentioned on pp. 59 in which the solution was stirred for 19 hours in an atmosphere of hydrogen was also done. The quantities used were:-

.85 gms. bisulphite compound.
25 cc. of water.
1.00 cc. of sodium bisulphite solution.

In this case however on exposing to the air and using an ordinary stirrer a further 24 hours stirring produced no salt out.

It was concluded therefore, that the compound formed by the action of sodium bisulphite solution on the pure sodium bisulphite compound is not oxidised on exposure to the air which is a result opposite to that obtained with the unpurified bisulphite compound.

Effect of Stirring.

This experiment was performed with the pure bisulphite compound but it has been described already (see pp.61).

Effect of Temperature on the Reaction.

As in many cases in the literature, Fierz David (loc. cit.); Woroshtzow (loc. cit.), the solution of the nitroso β-naphthol in the sodium bisulphite solution was carried out at 5° instead of 20°, as was done here, it was advisable to carry out an experiment at this temperature in order to find out if the production of non salting out solutions was confined to the higher temperature.

The results obtained showed that the reaction proceeded as easily at 5° as at 20°, non salting out being produced at 5° by adding exactly the same quantity of sodium bisulphite solution as was needed at 20°.

These experiments had shown that by the action of sodium bisulphite on the purified bisulphite compound it was possible to obtain a solution of the non salting out compound of a stable nature. It appeared therefore, that using these materials it might be possible to isolate this compound.

Attempt/

Attempt to Isolate the Compound formed by the Action of Sodium Bisulphite on the Bisulphite Compound of Nitroso β-Naphthol.

There appeared to be two methods by which isolation might be attempted.

(1) formation of an insoluble salt.

(2) crystallisation from a suitable solvent making use of the difference of solubility between the new compound and the ordinary bisulphite compound.

(1) As the solution contained sodium bisulphite it was necessary to use soluble salts of those metals which would not give a precipitate with this acid radical. After experiment Copper, Cobalt Magnesium, and Zinc nitrates were found to be suitable and 50% solutions were added to a solution made up by dissolving 2 gms. of the bisulphite compound in 1.83 cc. of a solution of sodium bisulphite whose strength was accurately known (see pp. 31).
This was made up by decomposing a known weight of A.R. sodium carbonate with sulphur dioxide. The solution prepared in this way had a concentration of 3.946 mol/litre. 2 gms. of the bisulphite compound and 1.83 cc. of sodium bisulphite solution of this concentration are equimolar quantities. In no case however, was a precipitate obtained even on cooling in ice.

(2) The first attempts to prepare the non salting out compound by this method were made in much the same way that the ordinary bisulphite compound would have been prepared. That is to say the bisulphite compound was dissolved in a quantity of water which easily dissolved it and then a quantity of the sodium bisulphite solution was added. The quantities used being equimolar. After standing for 12 hours an equal volume of alcohol (instead of half the volume as in the purification of the ordinary bisulphite compound) was added, and the solution cooled to 0° in ice. In spite of this extra addition of alcohol, however, no separation of any kind took place, the solubility of the new compound being evidently very much greater than that of the ordinary bisulphite compound.

The following modification was therefore introduced to counteract this. The sodium bisulphite was added directly to the bisulphite compound, and then water was added very gradually drop by drop during the course of two hours. In this way the new compound was formed in an absolute minimum of water.

Before giving the results obtained by using this procedure it will be necessary to give an account of the tests used to distinguish the ordinary bisulphite compound from any other which might be obtained.

These/

These tests were as follows.

(a) An analysis of the sodium content. The percentage of sodium in a monobisulphite compound of nitroso β-naphthol is 8.30%. In a dibisulphite compound 12.08% and in a compound formed by the union of one molecule of nitroso β-naphthol with three molecules of sodium bisulphite 14.22%.

(b) Dilute sulphuric acid (.5 N.) gives on warming a very characteristic reaction with the ordinary bisulphite compound. .01 gm. of the bisulphite compound dissolved in 10 cc. of half normal sulphuric acid, warmed and set aside, gives a strong yellow colouration within half an hour. More concentrated solutions give a deep red colour. In contrast to this, solutions of the bisulphite compound containing slightly more than an equimolar quantity of sodium bisulphite (and therefore presumably free of the ordinary bisulphite compound) do not give this colouration. In this case a precipitate of 1:2:4 acid is obtained which can be easily recognised. This precipitation is also a delicate test for the presence of a small quantity of the non salting out compound as a quantitative experiment showed that .01 gm. of bisulphite compound to which had been added an equivalent quantity of sodium bisulphite and the solution made up to 10 cc. with half normal sulphuric acid, gave, after/

after 24 hours an easily recognisable precipitate of 1:2:4 acid.

With these tests as a guide the following experiments were carried out:-

EXPT. 1.

2 gms. of the sodium bisulphite compound .007219 mol.
1.83 cc. of bisulphite solution .007228 mol.
3.5 cc. of water.

In this first experiment as nearly as possible equimolar quantities of the bisulphite compound and of sodium bisulphite were taken.

On adding an equal volume of R.S. alcohol and setting aside overnight at 0^{o} a precipitate of white feathery crystals was obtained but these were small in quantity; these were removed by filtration. Ether was then added to the filtrate till it became cloudy and it was set aside for another 24 hours. A fairly heavy precipitate of pure white crystals was obtained.

Both these compounds were then tested by the methods mentioned above.

The precipitate obtained from the alcohol gave a sodium content of 11.16%.

The sulphuric acid test gave a deep red colouration and no trace of 1:2:4 acid crystals.

In/

In the case of the precipitate obtained with ether the results were sodium 8.59% and a deep red colour and no crystals with sulphuric acid.

This would seem to show that the crystals obtained by addition of alcohol were probably a mixture of sodium bisulphite and the ordinary bisulphite compound. Those obtained from the ether almost pure bisulphite compound with a very small quantity of sodium bisulphite mixed with them.

EXPT. 2.

2 gms. of the bisulphite compound.

2.70 cc. of bisulphite solution.

A ratio of 1 mol. of bisulphite compound to approximately 1.5 mol. of sodium bisulphite.

Exactly the same procedure was adopted as in the previous experiment. In this case as in the previous one a white solid was obtained when alcohol was added, however, instead of a solid a yellow oil was obtained when ether was added. In the course of a few minutes however, this changed to a solid which on standing overnight became crystalline. The same tests were applied also. The results were. Sodium content 10.83% (alcohol precipitate) 9.13% (ether precipitate). The sulphuric acid test failed to produce any 1:2:4 acid in either case, only a deep red colouration. The deductions are similar to those made/

made before. The end products are only mixtures of the ordinary bisulphite compound with sodium bisulphite. The composition of the yellow oil is more fully discussed later.

EXPT. 3.

2 gms. bisulphite compound.

3.6 cc. bisulphite solution.

3.0 cc. water.

The ratio in this case is approximately 1 mol. of bisulphite compound to 2 mol. of sodium bisulphite.

A solid precipitate was obtained in this case also, with the alcohol, and a yellow oil with the ether. In this case the oil did not solidify on keeping it for several days. It was removed from the liquid from which it had been precipitated by means of a separating funnel and washed with ether several times. The ether was then removed at the pump at ordinary room temperatures, as it was found that sulphur dioxide was given off when the temperature was raised to 50°. The pale yellow oil was then placed in a vacuum desiccator over phosphorus pentoxide to remove water. During this stage which lasted for three days the oil became much darker and slightly green in colour. When it was found that the weight was almost unaltered after standing overnight the same tests as those used in the previous cases were applied.

The/

The solid obtained at the alcohol stage gave no colouration and no 1:2:4 acid but a strong smell of sulphur dioxide. As it was also found not to contain carbon it was concluded that it was sodium bisulphite. The oil gave a sodium content of 13.72% taking an average of several determinations and a big precipitate of 1:2:4 acid with dilute sulphuric acid. At the same time there was a strong smell of sulphur dioxide. From this experiment it might be concluded that the oil is the looked for compound. This is not at all probable as it was never found to have a sodium content of either 12.08% or 14.22% which would make it definitely a substance containing two and three atoms of sodium respectively. Figures as low as 12% and as high as 15% were found, which point to the oil being a mixture and not a compound.

The conclusions which can be drawn from these experiments will be summarised under the discussion of results (pp. 109) when some further facts which also have a bearing on this matter will be included. As this method did not appear to be any more successful than the previous one another method was tried.

Effect/

Effect of Adding Sodium Nitrate to a Solution of the Non Salting Out Compound.

The idea in using sodium nitrate instead of sodium chloride is of course quite clear. The solubility of sodium nitrate is about 87 gms./100 gms. water as against the 36 gms./100 gms. water of sodium chloride. By using sodium nitrate therefore a much greater concentration of sodium ions and hence a much greater salting out effect can be produced. In the actual experiment dry powdered sodium nitrate was used.

The following method was used:- 4 gms. of the bisulphite compound was dissolved in 7.2 cc. of bisulphite solution (1 mol. bisulphite compound to approximately 2 mols. of sodium bisulphite) with the addition of 7 cc. of water. This solution was divided into two portions. To the 1st half excess of sodium chloride was added and the solution stirred for 2 hours. No salting out took place. To the 2nd half whose volume was 7.5 cc. sodium nitrate was carefully added, when 4.45 gms. had been added the solution salted out. The solution was filtered and the pure white precipitate well pressed down and allowed to drain. It was then dissolved at the ordinary room temperature in the absolute minimum quantity of water. The volume of the solution was 8 cc. To this 8 cc. of/

of R.S. alcohol was added and the solution set aside overnight at 0°. The crystals obtained were washed with alcohol and ether and dried. They were feathery and pure white and weighed .588 gms.

.25 gm. of the crystals were dissolved in water and dilute sulphuric acid added. After 48 hours there was no trace of 1:2:4 acid and the solution had become dark red in colour. The remaining crystals were then dissolved in 10 cc. of half normal acid and exactly the same result obtained. These results indicate apparently quite conclusively, as will be shown, that the compound formed between the sodium bisulphite compound of nitroso β-naphthol and sodium bisulphite cannot exist except in solution. The proof is as follows:-

The weight of crystals obtained by recrystallising the salted out substance was .588 gms. This must represent less than the weight of crude substance salted out. Now it is shown that when this weight of crystals was treated with dilute acid no trace of 1:2:4 acid was obtained, therefore, from the quantitative figures given there must have been less than .02 gm. of substance which was not the ordinary bisulphite compound since .02 gm. of the compound formed between the sodium bisulphite compound and sodium bisulphite can be detected by this test. Therefore there must have been at least .568 gms. of the/

the ordinary bisulphite compound in the precipitate which was salted out. This was salted out from a solution whose volume was 7.5 cc. Now reference to the table given on pp.28 will show that the salting out time for a solution containing .586 gms. of bisulphite compound in 7.5 cc. of water is about 1 - 1.5 minutes. In actual fact it was found that this solution would not salt out, using sodium chloride.

Only one interpretation can be placed on this. The ordinary bisulphite compound obtained, cannot have been in solution as such, since if it had been, it would have salted out on the addition of sodium chloride. If it was not in solution as the ordinary bisulphite compound, it certainly was the ordinary bisulphite compound when it was precipitated as shown by the tests. In other words it must have changed during the salting out process, from one compound to another. If the process of salting out can decompose the unknown bisulphite compound there is not much hope of obtaining it in any other way, as the process of salting out is not one which could be considered to assist decomposition, quite the reverse.

Indirect/

Indirect Evidence of Constitution of the Compound.

When it was found that the isolation of the compound with a view to determining its constitution by the ordinary methods employed in organic chemistry was apparently impossible, a method which would not involve the actual separation and purification of the compound was sought for.

Such a method would be one by which the amount of bisulphite compound reacting with a known weight of sodium bisulphite could be determined. The amount of bisulphite compound present in a given solution can, as has been shown, be determined by observing the time which it takes to salt out under standard conditions, i.e. temperature, constant rate of stirring and equal weights of salt added. The method to be adopted was as follows. If a known volume of a sodium bisulphite solution whose concentration is known be added to a given weight of the bisulphite compound and the salting out time determined, a similar salting out time can be found for another solution of the bisulphite compound alone, without the addition of sodium bisulphite. As the amount of bisulphite compound in this second solution is known, the amount of unchanged bisulphite compound in the solution which had the sodium bisulphite added to it can be determined and hence the weight of bisulphite compound which has been/

been acted on by the sodium bisulphite.

The obvious advantage of this method is that only an approximate figure, as in the determination of empirical formulae, is needed, because the ratio must be a whole number, say, 1 mol sodium bisulphite to 2 mol of the bisulphite compound or 1 : 1 or some such whole number ratio.

As the method is somewhat novel the full results will be given.

EXPT. 1. Addition of sodium bisulphite solution to a known weight of bisulphite compound.

1.500 gms. bisulphite compound.
.500 cc. sodium bisulphite solution.
25.00 cc. distilled water.

Stirred at 20° for 10 mins. and allowed to stand 18 hours at room temperature 15°-20°.

10.00 gms. salt added to solution at 20° with constant stirring.

Time to salt out 6.0 mins.

EXPT. 2. Exactly as above but the solution was allowed to stand for 28 hours in order to insure that the reaction was complete in Expt. 1.

Time to salt out 6.0 mins.

The reaction can therefore be taken as complete in both cases.

Determination of Concentration of a solution of the Pure Bisulphite compound with a salting out time of 6.0 mins.

EXPT. 1.

.850 gms. bisulphite compound.

25.50 cc. water.

Conditions of salting out as in previous expts.

Time to salt out 8.0 mins.

EXPT. 2.

.900 gms.

25.50 cc. water.

Conditions as above.

Time to salt out 7.5 mins.

EXPT. 3.

.950 gms.

25.50 cc. water.

Conditions as above.

Time to salt out 6.0 mins.

This therefore is the concentration of the solution which had had Sodium bisulphite solution added to it.

The concentration of the sodium bisulphite solution used was 3.673 mol / litre.

∴ .500 cc. contain .001836 mol.

Now/

Now the weight of bisulphite compound unacted upon by this quantity of bisulphite as determined by the salting out time is .950 gm.

$\therefore$ Weight of bisulphite compound acted on = 1.500 gm. - .950 gm = .550 gm = $\frac{.550}{277}$ = .001986 mol.

.0018 mol of $NaHSO_3$ $\therefore$ reacts with .0020 mol of the bisulphite compound. The ratio is obviously 1:1.

This experiment was repeated with another quantity of the bisulphite compound but a similar result could not be obtained. This was traced eventually to the fact that this particular preparation of bisulphite compound had been prepared sometime previous to the experiment. Under these conditions it was found that the extra molecule of sodium bisulphite adds itself very slowly and as a result does not show its full effect in preventing salting out (see pp. 68) When a fresh preparation of the bisulphite compound was used however, very similar results were obtained.

Weight of compound taken 1.500 gms.
ccs. of sodium bisulphite added .500 cc.
Concentration of bisulphite solution 3.758 gm mol/litre.
Time to salt out 7.0 mins.

Weight/

Weight of bisulphite compound dissolved in 25.5 cc. of water which was found to salt out in 7.0 mins.

= .950 gms.

∴ Weight of bisulphite compound acted on

= 1.500 - .950 = .550 gms.

= .001986 gm. mol. or approx. .0020 gm. mol

∴ .0019 mol. of sodium bisulphite reacts with .0020 mol. of the bisulphite compound.

Figures which are very similar to those obtained in the 1st experiment.

Therefore as determined by this method the composition of the non salting out compound is 1 mol of $NaHSO_3$ + 1 mol of the sodium bisulphite compound of nitroso β-naphthol.

The possible constitution of this compound will be discussed under discussion of results.

Reactions of Methyl Nitroso β-Naphthol.

In order to determine if possible the position (as will be explained later) of the 2nd sodium bisulphite molecule it was decided that the behaviour of the methyl nitroso β-naphthol would have to be investigated. Some of the properties of this compound have already been determined by Woroshtzow (Ber 1929,

62/

62, 68) but for the present purpose it was necessary to extend the investigation very much further than he had done.

It was prepared according to the directions given by Illinski (Ber. 1884, 17, 2584) and on recrystallising from petroleum ether (60° - 80°) pure yellow crystals of m.p. 74° were obtained.

In giving an account of the behaviour of this compound towards sodium bisulphite it will not be necessary to give full details of the experimental procedure as this was exactly the same as with the ordinary nitroso β-naphthol so the results may be conveniently summarised as follows:-

(1) A solution which will salt out is obtained only when 1 mol. of sodium bisulphite for 1 mol. of the methyl compound is used.

(2) A non salting out solution is obtained when more than 1.5 mol. of sodium bisulphite is added to 1 mol. of the methyl compound.

(3) The non salting out solution behaves in exactly the same way as the non salting out solution of the ordinary pure nitroso β-naphthol bisulphite Compound. That is:

(a) it can be made to salt out by stirring, alone.

(b) it can be salted out by the addition of a little sodium hydroxide.

(4)/

(4) A solution made by adding 2 mol. of sodium bisulphite to 1 mol. of the methyl compound gives 1:2:4 acid in exactly the same way as the ordinary bisulphite compound does. The reaction however appears to go more slowly with the methylated compound. (The test for the identification of 1:2:4 acid is that given in Analysis of Dyestuffs - A.G. Green.)

(5) Using 3 mol. of sodium bisulphite to 1 mol. of methyl nitroso β-naphthol an oil was produced when this solution was treated in the same way as those with the ordinary nitroso β-naphthol.

It will be seen therefore, that in all essentials the methyl nitroso β-naphthol behaves in exactly the same way towards sodium bisulphite as the unmethylated compound. The significance of this will be discussed later (pps. 111-112).

Nitroso β-Naphthol.

Although a considerable amount of work has been done on nitroso β-naphthol (Fuchs, Ber 1875, 8, 1026; Stenhouse & Groves, J.C.S. 1877, 1, 47; Henriques, Ber. 1885, 18, 705; Illinski, Ber. 1884, 17, 2584; Goldschmidt, Ber. 1884, 17, 803; Groves, J.C.S. 1884, 45, 295; Sluiter, Ber. 1911, 44, 1837.) a great deal of it has been repetition of work previously carried out so that the number of facts relating to the properties of this compound is rather limited.

The connection between the properties of nitroso β-naphthol and the subject of this research, the behaviour of its sodium bisulphite compound, is much closer than might at first appear.

One of the first observations made during the course of this work was that the time of solution of the nitroso β-naphthol in the sodium bisulphite solution varied considerably. This is of course equivalent to saying that under certain conditions the sodium bisulphite compound was formed with great difficulty while at other times it was formed easily. As the effect is at times very great the cause was investigated. The experiments carried out to determine the cause will now be given.

Conditions/

Conditions Determining the formation of the Sodium Bisulphite Compound of Nitroso β-Naphthol.

Influence of free sulphur dioxide:-

The influence of sulphurous acid in the sodium bisulphite was found to be very great. The following table will give an idea of the magnitude of the effect.

The solution of sulphurous acid used contained 88 gms. H_2SO_3/litre which corresponds to a saturated solution at normal atmospheric pressures.

The stirring was carried out in a closed tube in order to prevent the escape of SO_2.

The suspension of nitroso β-naphthol and sodium bisulphite used was made up as given on pp. 47 . 25 cc. of this was used for each experiment.

TABLE 18.

No. of Expt.	cc. of H_2SO_3 added.	Time of solution.
1	0	5 mins.
2	1	25 mins.
3	5	24 hours.

With regard to No.2, although 25 mins. is given as the time of solution as denoted by a change from bright yellow to reddish brown, this change was not complete/

complete in 25 mins., a considerable number of the larger particles of nitroso β-naphthol still being bright yellow in colour.

In the case of No.3 there was not the slightest trace of change in colour so that to all intents the nitroso β-naphthol does not react with sodium bisulphite solution under these conditions.

If the stirring is carried out in an open beaker the nitroso β-naphthol will generally go into solution if sufficient time is given for the escape of sulphur dioxide. The addition of a little caustic soda, as recommended in Dye Chemistry, Fierz David, pp.50, by reacting with the free sulphur dioxide has the same effect although the reason is not stated in that text book.

The methyl nitroso β-naphthol is even more sensitive to sulphur dioxide and it would not go into solution if the slightest trace of free sulphurous acid was present. The sodium bisulphite solution therefore had to be carefully titrated with dilute sodium hydroxide, using methyl orange to show the point at which all free sulphurous acid had been removed, before it could be used to make the bisulphite compound of the methylated nitroso β-naphthol.

Effect of the Solution in which the Nitroso β-naphthol is precipitated, on the Solubility of the Nitroso β-Naphthol in Sodium Bisulphite solution.

In preparing the nitroso β-naphthol it is of course allowed to stand for some time, usually about 12 hours in an acid solution in order to complete nitrosation, this has already been explained. The concentration of hydrogen ions in this solution may vary considerably however, depending on how carefully the addition of acid has been made. The influence of a few drops of nearly 4 N. hydrochloric acid (such as was used) in raising the proportion of hydrogen ions just after the neutral point has been passed is very great. In this way it may come about that one preparation may stand in a comparatively strongly acid solution for 12 hours while another may stand in an almost neutral solution. On drying these two different preparations of nitroso β-naphthol it was found that on subsequent treatment with sodium bisulphite solution the one which had stood in neutral solution dissolved and formed a bisulphite compound much more readily than the other. In addition to this, washing an acid preparation with dilute caustic soda did not make the nitroso β-naphthol any more soluble in sodium bisulphite. Also the effect is not very noticeable unless/

unless the nitroso β-naphthol is actually dried before being treated with sodium bisulphite.

The solubility of Pure Nitroso β-Naphthol in Sodium Bisulphite Solution.

The pure nitroso β-naphthol used in this experiment was made by forming the sodium salt and decomposing with acid, Illinski (loc. cit.) This purification was carried out twice and the nitroso β-naphthol allowed to dry in air. Sufficient sodium bisulphite solution was then added to have effected solution with ordinary nitroso β-naphthol. About 1.2 mol./mol. nitroso β-naphthol is a convenient quantity.

It was found that under these conditions and stirring at 20° as usual, the pure nitroso β-naphthol is practically insoluble in sodium bisulphite solution. Even after 3 hours stirring the colour of the nitroso β-naphthol was still bright yellow, whereas if the unpurified form had been used the solution would have turned dark red brown in colour in five minutes time after the addition of the sodium bisulphite solution.

As it was found that the pure sodium salt of nitroso β-naphthol was very readily soluble in sodium bisulphite solution it was thought advisable to try the effect of (1) very carefully decomposing the/

the sodium salt with acid in order to have the minimum excess of acid when preparing the pure nitroso β-naphthol; (2) adding a small quantity of sodium carbonate solution to the pure nitroso β-naphthol solution. Both these measures were taken to try to ensure that it was not the action of acid on the nitroso β-naphthol which was causing the insolubility.

In both cases there seemed to be only a slight increase in solubility.

Solubility of "Brown" Nitroso β-Naphthol.

There is a form of nitroso β-naphthol which has not so far been mentioned but which will be dealt with more fully in the next section. This is a brown form which is obtained by dehydrating the freshly precipitated but unpurified yellow nitroso β-naphthol. For convenience, it will be mentioned in this section, rather than later, that it does not readily go into solution in sodium bisulphite.

A summary of the reaction between nitroso β-naphthol and sodium bisulphite therefore takes the following form.

Yellow unpurified, rapid formation of bisulphite compound.

Yellow unpurified, (neutral soln. and dried) rapid formation of bisulphite compound.

Yellow/

Yellow unpurified,(acid soln. and dried) slow formation of bisulphite compound.

Yellow purified very slow formation of bisulphite compound.

Brown dehydrated " " " " "compound".

All forms, in the presence of SO_2 no formation of the bisulphite compound.

It will therefore be seen that one of the reactions of nitroso β-naphthol is not its readiness, but rather its reluctance to form a bisulphite compound. This fact is not brought out in any of the literature.

The Colour of Nitroso β-Naphthol.

This may not appear to be of any great importance but it will be seen that among other things its investigation is justified on the ground that there is a relation between the colour and the behaviour of nitroso β-naphthol in quite a number of reactions.

"Brown" nitroso β-naphthol.

When freshly prepared nitroso β-naphthol is dried over calcium chloride or by gentle heat it changes in colour from bright yellow to browns of varying depth. This is recorded in nearly all the literature/

literature on the subject. Fuchs (loc. cit); Stenhouse & Groves (loc cit); Henriques (loc cit); Illinski (loc. cit); Goldschmidt (loc cit); Groves (loc cit); Sluiter (loc cit).

During the course of this investigation however, it was observed that the brown colour which the nitroso β-naphthol usually assumes on drying, did not appear if the drying process was carried out over sulphuric acid instead of calcium chloride or phosphorus pentoxide. It was further ascertained that the nitroso β-naphthol remained yellow for a considerable time if dried over calcium chloride provided an atmosphere of hydrochloric acid gas or sulphur dioxide was maintained in the desiccator.

A further experiment on the action of acid in preventing the formation of the brown compound was carried out as follows. A preparation of nitroso β-naphthol was made and acid was added till the solution was strongly acid. The nitroso β-naphthol was allowed to stand in this solution for 12 hours. A similar preparation was made, but in this case only sufficient acid to ensure the presence of free nitric oxide to complete the nitrosation, was added. The two preparations were then filtered off, washed and placed in a vacuum desiccator over calcium chloride. Within/

Within 24 hours the non acid preparation had gone brown in colour while the nitroso β-naphthol which had been allowed to stand in acid solution was still bright yellow.

It was further found that if the non acid nitroso β-naphthol was allowed to stand without intensive drying it gradually lost the property of becoming brown when intensively dried. In other words it reverted to the acid prepared type.

Colour of purified uncrystallised Nitroso β-Naphthol.

Illinski has shown (loc. cit.) that nitroso β-naphthol purified by forming the sodium salt and decomposing this with dilute acid does not assume a brown colour on drying but remains bright yellow. This was verified and his result was made more certain by actually estimating the percentage of nitroso β-naphthol present in a sample, after drying over phosphorus pentoxide. The estimation was made by means of titanous chloride solution. (Knecht and Hibbert, New Reduction Methods in Volumetric Analysis 2nd Edition 1925, the method recommended for nitroso compounds (see pp. 32 and 95) was not used, however, as the colour change is not sharp, instead a known excess of titanous chloride was added and allowed to stand at room temperature. The excess was/

was then titrated with the iron alum solution and hence the volume of titanous chloride used is obtained. This is the method recommended for nitro compounds

This estimation gave (1) 99.77%

(2) 99.85%

The difference of .2% can be accounted for by experimental error. It should be noted then, in view of what will be said in the next section on the composition of "brown" nitroso β-naphthol pp.100, that pure uncrystallised nitroso β-naphthol can be pure yellow in colour.

The Colour of Crystalline Nitroso β-Naphthol.

Nitroso β-naphthol has been crystallised by the following workers and described as follows:-

(1) Fuchs (loc. cit.) crystallised by dissolving in benzene and adding ligroin

reddish yellow crystals m.p. 110°.

(2) Stenhouse and Groves (loc. cit.) crystallised from several solvents:- alcohol, ether, benzene, carbon disulphide and petroleum

thick prisms orange brown in colour m.p. 109.5°.

(3)/

(3) Illinski (loc. cit.)

(As this was purified by distillation in steam it was probably hydrated) Described as pure yellow needles m.p. 106°.

(4) Sluiter (loc. cit.)

(This was purified very carefully for conductivity measurements by "shaking many times with benzene and precipitating with ligroin)" brown compact crystals m.p. 112°.

Up till the present therefore it will be seen that the "pure" nitroso β-naphthol had always a red or reddish brown colour; in fact Sluiter (loc. cit.) describes it as brown nitroso naphthol in contrast to β-nitroso α-naphthol which he calls yellow nitroso naphthol and the 4 nitroso 1 naphthol which he calls white.

It was noticed, however, that the nitroso β-naphthol which had been twice purified by conversion into the sodium salt gave crystals of a very light reddish brown colour when crystallised from ligroin, in fact they might almost have been described as yellow brown. The suspicion that the real colour of nitroso β-naphthol was not red was intensified when on crystallising very slowly from ligroin a few yellow crystals were obtained, of minute size. Further crystallisations failed to produce any larger yield so/

so it was decided to try sublimation, as it was noticed during the course of doing melting points that the nitroso/β-naphthol showed indications of subliming.

The sublimation was carried out at 20 mm. pressure and 100°. This temperature was probably rather on the high side; 90° - 95° would probably be better as it was noticed that as the sublimate grew thicker and the outer layers further from the cold surface they tended to become darker yellow in colour, indicating a tendency to form the red type of crystal.

By subliming only a small quantity at a time, however, pure bright yellow needle-shaped crystals were obtained.

Quite apart from this experiment which appears to show that the true colour of crystallised nitroso β-naphthol is yellow, previous workers with this compound all seem to have missed the remarkable fact that it is only the surface of the crystals which are red or brown in colour. If the reddish brown crystals which are obtained by crystallisation from ligroin are crushed, a yellow powder is obtained and if a single broken crystal is examined the interior is seen to be bright yellow. It was thought at one time that these might be two different forms as in the well known case of mercuric iodide which can be made to change from yellow to red when near its transition temperature, merely by pressure. This theory was abandoned,/

abandoned, however, when it was found that the melting points of the crystals were the same before and after crushing.

The melting points (which were accompanied by decomposition in every case, but were sharp) of various types of crystals were observed on a thermometer reading $\frac{1}{10}^{\circ}$. After applying stem correction these were found to be:-

(1) Yellow (sublimed) 106.7°

(2) Red (once purified by sodium salt method and crystallised from hot ligroin) 108.5°

(3) Pale red (twice purified by sodium salt method and crystallised from ligroin 25° to -12°, in order to avoid any decomposition of the crystals by heat) 108.0°

(4) Yellow (No.3 crushed - see above) 108.0°

Colour of Methyl Nitroso β-Naphthol.

This compound in contrast to the unmethylated nitroso β-naphthol showed no tendency to develop a red colour on crystallisation, or, to be more accurate, on heating, for it can be seen from the results already given that the red colour is developed whenever the nitroso β-naphthol is heated. Crystallisation involves heating to a greater or less extent. This difference/

difference in behaviour is of some importance and will be dealt with in the discussion of results.

Reactions of Brown Nitroso β-Naphthol.

The reactions which the brown form of nitroso β-naphthol prepared in the way given on pp.93 gives are of importance and will now be described and the results summarised in the discussion of results.

(1) It has generally been assumed up to date that this substance is pure anhydrous nitroso β-naphthol. Illinski (ibid) says of this: "Closer investigation showed that the brown needles likewise were nitroso β-naphthol". Unfortunately he does not say what the nature of his closer investigation was. However an independent investigation was carried out as follows.

The nitroso content of a yellow unpurified sample was estimated by titanous chloride as before and the water in an exactly similar sample was estimated by dehydrating in a vacuum desiccator till loss of weight ceased.

The figures obtained in two cases, one, with fairly dry nitroso β-naphthol and the other with a moist paste were:-

1./

1.	Nitroso β-naphthol by titanous chloride	16.82%
	" " " drying	15.30%
	Difference	1.52%
2.	Nitroso β-naphthol by titanous chloride	92.55%
	" " " drying	91.20%
	Difference	1.35%

This is greater than can be accounted for by experimental error.

The significance to be attached to these figures is that the nitroso β-naphthol is apparently giving up, on drying, more water than it contains, assuming the figures obtained by the titanous chloride to be correct, and as this method has given good results in another case (see pp.96) there is no very good reason to doubt that they are not correct here also.

(2) The observation made by Stenhouse and Groves, (Ann. Chem. Pharm. 189, 145, 1877) that no satisfactory yield of nitroso β-naphthol was obtained by decomposing with acid the alcoholic sodium hydroxide solution of the brown nitroso naphthol was verified.

On the other hand the cobalt salt of nitroso β-naphthol was readily formed by the addition of a salt of cobalt to the acetic acid solution of the brown nitroso β-naphthol. Illinski & Knorre, (Ber. 1885, 18, 699)

(3)/

(3) The melting point was found to be 107.0° which is .9° lower than that of the pure yellow uncrystallised variety.

(4) On the addition of ligroin to a benzene solution of the brown nitroso β-naphthol a purple amorphous substance was precipitated. This was not given, or only in minute quantity, by the pure yellow and yellow hydrated varieties, so that it is probable that the purple compound is the brown "nitroso β-naphthol" separated from the yellow. This is probably the same substance as was obtained by Illinski (loc. cit.) and which he found impossible to purify for purposes of identification. Unfortunately it has also been found impossible to purify it in this case. It is insoluble in water, ligroin and petroleum ether, fairly soluble in alcohol and readily soluble in benzene and pyridine, especially the latter. In no case, however, could it be crystallised.

In addition to this difficulty of purification which could not be overcome, the quantity obtained was very small, since the brown compound seems to be merely a surface product which protects the rest of the nitroso β-naphthol from further dehydration. This can be seen by examining the nitroso β-naphthol through a microscope. Grinding up the nitroso β-naphthol did not greatly increase the yield, because,

as/

as has been pointed out elsewhere, unless the dehydration is started immediately after formation, the nitroso β-naphthol becomes "fixed" in the yellow form.

For reasons which will be explained later (pp. 117) some of the purple compound was dissolved in absolute alcohol and saturated with dry hydrochloric acid gas under slight pressure. After 24 hours the tube containing the solution was set aside for a further 24 hours at 0°. The only change which was observed was in the colour of the solution which changed from deep red to an equally intense violet.

A further quantity of the compound was extracted with petroleum ether to remove any nitroso β-naphthol which might be present. It was then dried and boiled with water. The solution which was at first colourless gradually assumed a yellow colour similar to that given by nitroso β-naphthol itself. On adding acetic acid and a cobalt salt a precipitate of the cobalt salt of nitroso β-naphthol was obtained. This reaction is also discussed (pp. 117).

Effect of Light on Nitroso β-Naphthol.

It now only remains to consider the effect of light on nitroso β-naphthol. This is the question referred to on pp. 40. The effect was noted during

one/

one of the experiments carried out in order to find a method for producing a solution of constant salting out time. The details of the experiment will be found on pp.39 but an outline will be repeated here. The nitroso β-naphthol was made in the usual way, it was carefully washed free from chlorides and acid, and dried by exposure to the atmosphere at room temperature. It was found to be 91.01% nitroso β-naphthol and in this condition was a bright yellow, apparently perfectly dry powder. Small quantities (2.600 gms.) of this powder were then dissolved in varying quantities of sodium bisulphite and salted out. When a repetition of these experiments was tried a day or two later, however, it was found that although using exactly the same quantities, the salting out times had changed completely, a solution which had in the first case salted out in 28 mins, in the second case took 65 mins.

After as far as possible taking everything into consideration the conclusion was reached that light must be the cause of this change. An experiment was undertaken to prove this. Two separate preparations of nitroso β-naphthol were made and samples were taken from each, one being kept in the dark and the other exposed in a water cooled tube to sunlight for about 10 hours.

TABLE 19./

TABLE 19.

No. of Prep.	How kept.	Salting Out times.
(1)	dark	16 mins.
	light	43 mins.
(2)	dark	31 mins.
	light	100 mins.

It can be seen from these results that exposure to light in some way affects the nitroso β-naphthol as regards the subsequent formation of a salting out form of the bisulphite compound.

These constitute the observations made on nitroso β-naphthol itself, and they will shortly be discussed and a theory advanced which it is hoped may introduce some meaning into a mass of apparently, for the most part, unconnected facts.

DISCUSSION OF RESULTS.

The Process used for the Production of the Sodium Bisulphite Compound.

Dealing first with the absolutely practical side of the subject of this research, there is little to say. The reason for the non production of good yields is now very apparent. One might even go so far as to say that the problem is one of psychology rather than chemistry. That is to say, it must be remembered that there is no great difference in the initial stages of the preparation of 1:2:4 acid and the sodium bisulphite compound of nitroso β-naphthol. It is conceivable that mistakes might occur in the amount of sodium bisulphite added. The addition of the amount of sodium bisulphite necessary for the production of 1:2:4 acid, is, of course, fatal if the bisulphite compound of nitroso β-naphthol is the required product. It has been pointed out (by Dr Bain who was in charge of this process at the British Dyestuffs Corporation) that this is a most unlikely mistake in a large scale preparation. This is obviously the case, but it can also be pointed out that out of a very large number of preparations of this compound made under all conditions in the laboratory no single one ever failed to salt out when/

when this matter was carefully attended to. The facts of the matter are decisive on this point.

Leaving this source of error aside, however, there are two other points for the successful production of this compound which should be noted:-

(1) A large excess of acid in the preparation of the nitroso β-naphthol, followed by sodium sulphite to neutralise it, must be avoided.

(2) The addition of salt, immediately after the bisulphite compound has been formed, is inadvisable.

It is not necessary to explain (1) any further, it has been fully explained on pp. 38.

(2) refers to the observation (pp. 63) that a solution saturated with salt does not recover from a non salting out condition to the same extent that one which has not had salt added to it, does. As it is desirable to have as much as possible of the bisulphite compound in the salting out form, and as in making it more bisulphite is added than is theoretically necessary to form this compound, it might be as well to allow the solution to stand exposed to the air for some time before adding the salt. In this way any of the "di" bisulphite compound formed would be oxidised back to the "mono" or salting out form.

The complete explanation of this oxidation effect/

effect appears to be a problem of very great difficulty. It is quite evident that it must be due to some bye product, formed in the preparation of the nitroso β-naphthol bisulphite compound, since the effect does not appear when the purified bisulphite compound is used. What this substance could be it is impossible to make even a conjecture. In the preparation of nitroso β-naphthol a certain amount of resinous material is always formed, as it is also, when the nitroso β-naphthol is dissolved in sodium bisulphite. It would be necessary therefore to carry out an investigation of these tars which would be an extremely difficult, if not impossible, task.

The question of the effect of allowing the nitroso β-naphthol to stand in acid solution (pp. 35) might be dealt with here. It hardly enters into the practical side of the question as the effect is so small, taking the time needed for the change into consideration.

A satisfactory answer to this question is also somewhat difficult, but noting the similar increase in salting out time observed in the case of an alkaline solution, and knowing definitely that the nitroso β-naphthol is decomposed in an alkaline solution, it rather looks like a simple case of decomposition of the nitroso β-naphthol by the acid solution.

The Compound formed by the action of excess of Sodium bisulphite on Nitroso β-Naphthol.

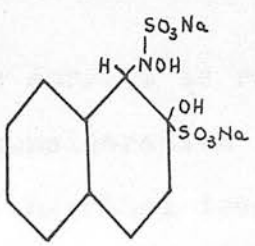
There can be no doubt now, that such a compound is formed, but it must be extremely unstable. This might be expected, however, the work of Fuchs and Elsner (loc. cit.) having shown this in the case of the bisulphite compound of resorcinol, for instance. Fuchs and Pirak (Ber. 1926, 59, 2454) also found that in the case of 4 amino α-naphthol, a bisulphite "compound" was obtained which was really a mixture of the amino naphthol bisulphite compound and sodium bisulphite, this seems to be a type of additive bisulphite compound very similar to the compound at present under examination. It is quite evident from an examination of the results obtained from the "oils" (pp.76), that the oil contains the true "dibisulphite" compound, as it will now be called, mixed with sodium bisulphite. The production of 1:2:4 acid with dilute sulphuric acid shows the presence of the dibisulphite compound, the high percentage of sodium indicates the presence of mixed sodium bisulphite. Also, the dibisulphite compound is only formed, or can only appear, as a dibisulphite compound in the presence of excess of sodium bisulphite, the less excess bisulphite the more readily does it revert to the ordinary bisulphite compound. This is quite evident/

evident from the results of the three experiments given, which show that the smaller the quantity of sodium bisulphite present the more readily did the yellow oil become a white solid which was the ordinary bisulphite compound, as shown by the tests applied.

Further, that the bisulphite compound can never exist in a solid or even liquid state is shown conclusively from the salting out with sodium nitrate experiment (pp. 77).

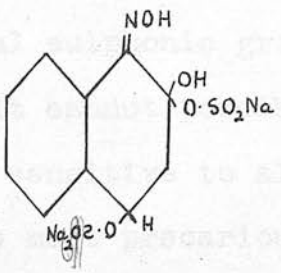
Under these circumstances, the use of the salting out time method (pp. 80) for determining the composition of the second bisulphite compound, is justified, as there is no hope of obtaining the compound other than in solution. The method is fully explained in the place mentioned.

The experiments made with the methyl nitroso β-naphthol were undertaken in order to determine if possible the position of the second bisulphite molecule. There are two likely positions. There is the possibility of addition to the doubly linked nitrogen, to give a structure similar to that shown in I (pp.16), in this case the molecule would be



I

Or there is the other possibility of the bisulphite molecule adding itself to the ring, as in several other cases of hydroxy compounds which have been mentioned (pp. 11). The position in the ring would probably be the 4 position as this would involve little change when the transformation into 1:2:4 acid takes place. It is not very likely that the group would go into say the 5, 6 or 7 position and then be eliminated altogether, or jump into the 4 position, when dilute acid is added. Of course there is no direct evidence that it is the 4 position which it occupies, but taking the facts mentioned into consideration, it seems the most reasonable. On this supposition therefore, the molecule would have the form



II

Which of these is correct is rather difficult to say, but taking into consideration the behaviour of the methyl nitroso β-naphthol towards bisulphite, II, is probably correct. The methyl nitroso β-naphthol behaved/

behaved towards bisulphite in exactly the same way as the unmethylated compound, now in order to form such a compound as I, according to Woroshtzow's theory (extended to oximes, it must be admitted) the NOH group would have to become an NO or nitroso group, the hydrogen atom removing itself to some other part of the molecule. The bisulphite molecule would then add itself on as it does to the ketonised hydroxy group. The methyl compound could not behave in this way and yet it forms a dibisulphite compound. (It may be as well to repeat here what has been said before that Illinski (Ber.1884, 17, 2584) has shown that the methyl compound has the oxime and not the nitroso structure.) The supposition therefore is that the second bisulphite group goes into the 4 position leaving the oxime group undisturbed.

The actual form taken by the group, that is, whether it is a real sulphonic group or not, can be answered easily. It cannot possibly be a sulphonic group. It is very sensitive to alkalies and its hold on the ring is most precarious, and, quite apart from this, if we suppose it occupies the 4 position, it is changed into a real sulphonic group on the addition of acid and therefore cannot have been one originally.

This is the last point which needs discussion in the case of the dibisulphite compound, the analysis and/

and structural formula of the new compound having been dealt with, but the opinion might be expressed that it is probable that in all the cases mentioned in the introduction, where nitroso phenols and naphthols are said to give sulphonic acids on treatment with sulphite or bisulphite and acid, a reaction similar to the one above takes place. To prove this, however, would possibly be very difficult, the stability of intermediate products would be almost certainly very small as in this case of nitroso β-naphthol. The observations on nitroso β-naphthol must now be considered.

Nitroso β-Naphthol.

The obvious point in the observations made on this compound is the relation between, solubility in sodium bisulphite, colour, and the action of acid. It will be noticed that all those preparations which showed a tendency to remain yellow did not form bisulphite compounds readily. Also, whenever acid of any description, whether present during drying or present in the sodium bisulphite, was included, the nitroso β-naphthol remained yellow and would not form its bisulphite compound.

This suggests that there may be two forms of nitroso β-naphthol, one which is formed in presence of/

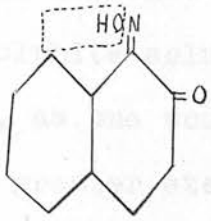
of acid or is stable in presence of acid, and insoluble in sodium bisulphite, and another which is soluble in sodium bisulphite and is formed in the absence of acid.

The significance of the colour must now be considered more closely. The point to be noticed here is the change in colour on drying, in the absence of acid. The nitroso β-naphthol becomes brown, which is supposed to be its natural colour, but it has been shown that this brown nitroso β-naphthol contains a substance which the yellow variety does not (pp. 102). It has also been shown that in order to assume this brown colour the nitroso β-naphthol loses more water than it apparently contains (in the form of free water) pp.101. This seems a very important point. In other words, can a mechanism be found which can explain how nitroso β-naphthol can give up water from its own unhydrated state, and it should be noted that another structure must also be found which is incapable of giving up water, for, as has been said, nitroso β-naphthol remains yellow on dehydration, under certain conditions mentioned above (pp. 94)? The point at which water can be split off from the molecule is most likely to be its least stable group, and this is the oxime group.

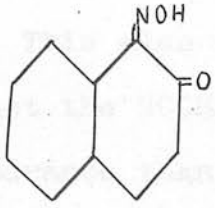
By writing the formula in the two following ways

it/

it can be seen how water can be spit off in one case and not in the other



I.



II.

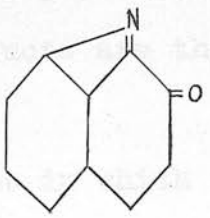
I. therefore, would be the form which would give water and II would be the form which would not and thus form II would be the form stable in the presence of acid.

This theory also explains the formation and non formation of bisulphite compounds. Woroshtzow has noted that the formation of bisulphite compounds may be prevented by steric hindrance (Bulletin de la Société Chimique à Paris 1924. 35 , 996.) and this seems to be a case in point. On looking at the two formulae given it is easily seen that in the case of II there might be some difficulty in the bisulphite molecule adding itself, because of the position of the NOH group, while no such obstacle occurs in the case of I. Now II has already been assigned to the yellow form stable in the presence of acid, and it is just this form which gives nitroso β -naphthol preparations which do not give, or give with great difficulty, sodium bisulphite compounds. It should also/

also be remembered that the methyl nitroso β-naphthol was especially sensitive in this respect to the action of acid, (in its case the presence of sulphurous acid in the bisulphite solution). This also fits in with the theory, as one would expect the $NOCH_3$ group to offer even greater steric hindrance than the NOH group.

The insolubility of the brown nitroso β-naphthol in sodium bisulphite might be mentioned as being against this theory, as in its case it would be expected that a large proportion of the NOH groups would be in the position shown in formula I, pp.115, but it is probably only a question of delayed solution, due to the presence of the brown substance which is itself insoluble, or nearly so, on the surface of the true nitroso β-naphthol.

The question of the constitution of the brown, or more correctly purple compound, since this is its colour when separated by benzene and ligroin from the nitroso β-naphthol from which it is formed, must be dealt with. On the theory given, it should have the constitution



The evidence for its formation is all indirect, since it has never been isolated in the pure state for reasons which have been explained. The following points should be noted, however, nitroso β-naphthol is yellow in colour; methyl nitroso β-naphthol shows no tendency to assume a red or brown colour.
In addition, it has been shown that while the brown compound does not give the sodium salt of nitroso β-naphthol in alkaline solution it gives the cobalt salt in acid solution. This could be explained by using the theory already given, that an acid solution turns the oxime, or potential oxime group, away from the 8 position and therefore makes it free to form addition products. An alkaline solution having the opposite effect. Also, when boiled with water the purple compound gives a yellow solution similar to that given by nitroso β-naphthol, this is even after it has been repeatedly extracted with ligroin to remove nitroso β-naphthol. Simple addition of water explains this reaction. The use of titanous chloride cannot for obvious reasons give any results other than indicate pure nitroso β-naphthol (since the reduction products are the same) this was found to be the case.

The experiment in which the solution of the purple compound was saturated with hydrochloric acid gas/

gas (pp.103) was carried out as an extension of the cobalt salt and boiling water experiments mentioned above. It was hoped to obtain /3-naphaquinone chlorimide by direct addition, this being a compound which could have easily been identified, and at the same time its formation could only have been explained by accepting the above formula. It was unfortunately unsuccessful.

There remain several points in connection with nitroso /3-naphthol yet to be cleared up, the action of light for which some results are given is an example. This cannot be as yet explained, and the whole subject of the structure and reactions of nitroso /3-naphthol threatened to become so wide that it was felt that it must be left alone for the present. Those parts affecting the formation of the bisulphite compound having been investigated according to the original plan.

Finally I would like to thank Dr David Bain for suggesting the subject and for the advice which he has given.
